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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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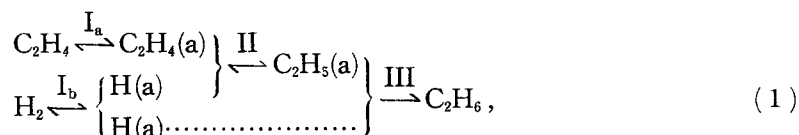
#### Abstract

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 C<sub>2</sub>P<sub>6</sub> (P: protium) was predominantly formed at the initial stage of reaction of C<sub>2</sub>P<sub>4</sub> with D<sub>2</sub>, similarly to the previous case of an evaporated copper film, while the ratio of the evolution rate of P<sub>2</sub> 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<sup>1,2)</sup> to proceed *via* a set of steps as



where step I<sub>b</sub> or III is rate-determining at temperatures below or above the so-called optimum temperature, respectively, so far as step I<sub>a</sub> is assumed so fast as to be nearly in equilibrium. Ethylene hydrogenation on nickel film freshly evaporated, however, has been found<sup>1)</sup> to accompany dissociative

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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 theory<sup>3)</sup> applied previously<sup>4)</sup> 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 catalyst<sup>4)</sup>.

### Experimental

Catalyst used was a nickel film evaporated, similarly as described in previous paper<sup>5)</sup>, under a vacuum of  $3 \times 10^{-7}$  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 cm<sup>2</sup>. 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 usual<sup>6)</sup> 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 found<sup>5)</sup> to give reproducible hydrogenation activity; however, the reaction on film F accompanies considerable dissociative adsorption of ethylene which results in the self-hydrogenation of ethylene<sup>1)</sup>. Film F once used for hydrogenation and subsequently outgassed *in vacuo* at the reaction temperature (signified by S) is known<sup>1)</sup> 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<sup>4,5)</sup>.

### Calculation of Unidirectional Rates of Elementary Steps

The rates of steps of scheme (1) can be evaluated by applying the previous method<sup>4)</sup> 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<sup>2)</sup>.

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

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

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 previously<sup>4</sup>).

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  $\phi$  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 method<sup>4</sup>).

### Results and Discussion

*Reaction of C<sub>2</sub>P<sub>4</sub> with D<sub>2</sub>.* Reaction was carried out at temperatures from 79 to 150°C with an equimolar mixture of C<sub>2</sub>P<sub>4</sub> and D<sub>2</sub> 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, A<sub>0</sub>, is predominantly formed and P<sub>2</sub> is evolved slower than PD except at the lowest temperature, 79°C. In the case of copper catalyst<sup>4</sup>), P<sub>2</sub> 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 method<sup>4</sup>) from the evolution rates of P<sub>2</sub> 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 C<sub>2</sub>P<sub>4</sub> with equimolar D<sub>2</sub> on Ni film R.

Temp. (°C)	Hydrogenation, V <sub>s</sub> (mmHg/min)	Hydrogen (%/min)		Ethylene (%/min)			Ethane*) (%)		
		P <sub>2</sub>	PD	E <sub>1</sub>	E <sub>2</sub>	E <sub>3</sub>	A <sub>0</sub>	A <sub>1</sub>	A <sub>2</sub>
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

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(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<sub>b</sub> and, consequently,  $y_1(H)$  should be equal to  $y_1(A)$  as observed with copper catalyst<sup>4</sup>. 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-CO<sub>2</sub> is RNW exposed to *ca.* 6 mmHg CO<sub>2</sub> 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 carbided<sup>7</sup>. According to the previous results<sup>1)</sup> 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-CO<sub>2</sub> 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-CO<sub>2</sub>, CO<sub>2</sub> 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 <sub>2</sub>	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  $\text{I}_b$  are evaluated according to Eqs. (5), (7) and (9). In the previous paper<sup>4)</sup> 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  $\text{I}_b$  because of the presence of side reaction mentioned above. A true rate of step  $\text{I}_b$  can be evaluated as follows. Irrespective of the presence of the side reaction of step  $\text{I}_b$ , 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  $\text{I}_b$  is rate-determining. Step II is evaluated to be far faster than hydrogenation rate,  $V_s$ , similarly to the case of copper catalyst<sup>4)</sup>, while the rate of step  $\text{I}_a$  is relatively small, as compared with the case of copper catalyst. *Reaction with a mixture of  $\text{C}_2\text{P}_4$ ,  $\text{C}_2\text{D}_4$ ,  $\text{P}_2$  and  $\text{D}_2$ .* In order to make sure the above conclusion on the rates of respective steps, the reaction with equimolar  $\text{C}_2\text{P}_4$ ,  $\text{C}_2\text{D}_4$ ,  $\text{P}_2$  and  $\text{D}_2$  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

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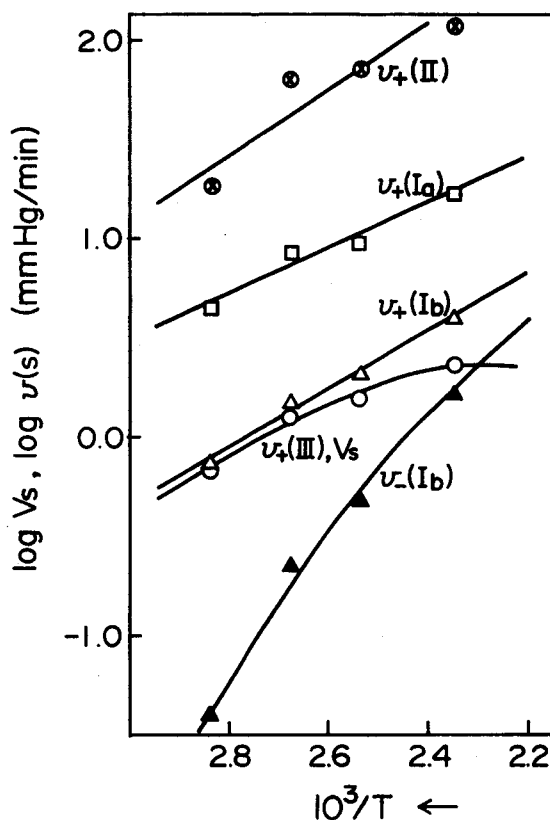


Fig. 1. Arrhenius plots of the rates of hydrogenation and elementary steps at 20 mmHg of initial partial pressures of ethylene and deuterium.

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 catalyst<sup>4</sup> 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 catalyst<sup>4)</sup> 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.

KEMBALL<sup>5)</sup> has observed that the rate of ethylene hydrogenation over evaporated nickel film at  $-120 \sim -100^\circ C$  is independent of ethylene partial pressure,  $P_E$ , and proportional to 0.5th power of hydrogen partial pressure,  $P_H$ . According to MASUDA<sup>6)</sup> the rate of ethylene hydrogenation over nickel

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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 catalyst<sup>9</sup>. 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 number<sup>10</sup>, 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  $-100^\circ\text{C}$ , 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 KEMBALL<sup>8</sup>. 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 MASUDA<sup>6</sup>. 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 papers<sup>2</sup>, because  $v_-(I_{b2})$  estimated from the difference between  $y_1(\text{H})$  and  $y_1(\text{A})$  is several times larger than  $v_+(I_{b1})$ .

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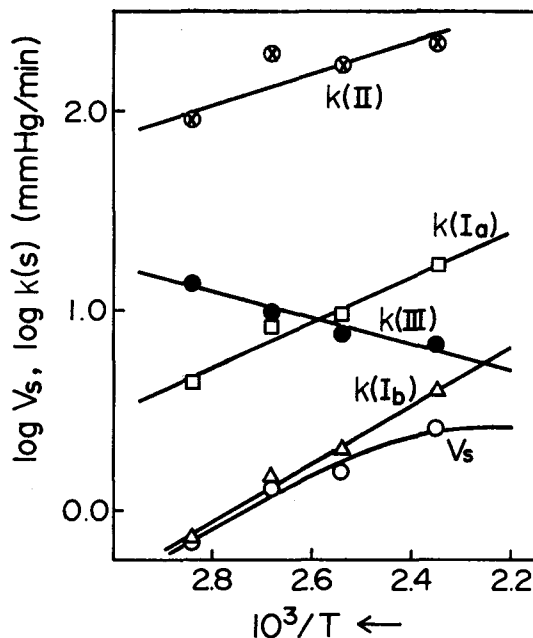


Fig. 2. Reaction structure of ethylene hydrogenation on Ni.  
 $P_E = P_H = 20$  mmHg.

The reaction structure<sup>3)</sup> 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<sup>1,2)</sup>.

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