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## REACTION STRUCTURE OF ETHYLENE HYDROGENATION ON METALLIC CATALYSTS

### Part 1—The Reaction on Evaporated Copper Film

By

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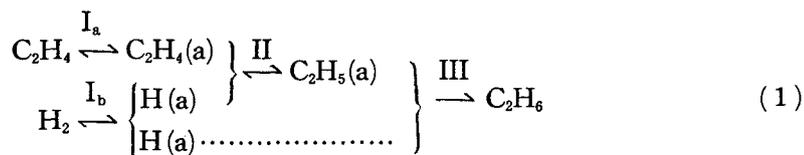
#### Abstract

The rates of elementary reactions constituting ethylene hydrogenation over an evaporated copper film were evaluated on the basis of experimental results of the reaction traced by deuterium. Hydrogenation rate increased monotonously with rise of reaction temperature from 78 to 135°C, distinctly differing from the cases of nickel and other transition metal catalysts which show the so-called optimum temperature, beyond which hydrogenation rate decreases.

It was concluded that with rise of reaction temperature beyond *ca.* 80°C a rate-determining step of hydrogenation changes from dissociative adsorption of hydrogen to surface reaction of hydrogen atom with ethyl group to form gaseous ethane, similarly to the case of nickel catalyst. On the basis of this conclusion, a consistent interpretation was given on kinetics of ethylene hydrogenation ever observed with copper catalyst.

#### 1. Introduction

Ethylene hydrogenation on nickel and other metal catalysts has been investigated<sup>1)</sup> in detail by the use of deuterium as a tracer and reaction mechanisms ever proposed for ethylene hydrogenation on various metal catalysts have been critically reviewed<sup>2)</sup>. The following HORIUTI-POLANYI's associative mechanism<sup>3)</sup> was found to be effective for the steady hydrogenation of ethylene over most of transition metal catalysts and a rate-determining step of hydrogenation was concluded to change from I<sub>b</sub> to III with rise of reaction temperature beyond the so-called optimum temperature.



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This conclusion, however, is much influenced by the presumptions of mechanism that step  $I_a$  of scheme (1) is extraordinarily fast to be nearly in equilibrium and that activation heats of respective steps are not affected by coverage of the catalyst surface. Ethylene hydrogenation over nickel, iron, tungsten and other metal catalysts was found, furthermore, to be accompanied often by side reactions resulting in ethane formation<sup>1)</sup>, *e. g.*, the self-hydrogenation of ethylene caused by dissociative adsorption of ethylene and hydrocracking of polymerized products. The presumptions and conclusion mentioned above were examined in the present work with copper catalyst.

A theory to discuss a steady rate of ethylene hydrogenation on the basis of relative rates of constituent steps has been developed by HORIUTI<sup>4)</sup> and others<sup>2,5,6)</sup>. According to the theory a reaction structure, *i. e.*, relative rates of respective steps at various temperatures can be determined experimentally on the basis of observed deuterium distributions in the products of ethylene deuteration but it has not yet been studied on account of experimental difficulties to exclude the side reactions and to make a quantitatively reproducible observation.

In the present work the analysis of reaction structure was investigated with ethylene deuteration over an evaporated copper film. Copper is known as one of less active catalysts for hydrogenation of olefin and ethylene hydrogenation over copper was found to proceed practically by scheme (1) alone and to give a sufficiently reproducible result of observation.

## 2. Theory

The theory of reaction structure analysis is reproduced so far as the mechanistic analysis of the present work is concerned.

### 2-1. Evolution rates of deuterio-substituted species during ethylene hydrogenation

By denoting protium and deuterium by P and D, respectively, evolution rates of deuterio-substituted species during a reaction between  $l$ -fold deuterated ethylene  $C_2P_{4-l}D_l$  ( $l=0, \dots, 4$ ) and  $m$ -fold deuterated hydrogen  $P_{2-m}D_m$  ( $m=0, 1, 2$ ) can be expressed as follows in terms of the forward and backward unidirectional rates,  $v_+(s)$  and  $v_-(s)$ , of step  $s$  in scheme (1), where the isotopic differences of rates are ignored.

Hydrogen :

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$$\left. \begin{aligned} V^{P_2} &= y_0^2 v_-(I_b) - Y_0 v_+(I_b), \\ V^{PD} &= 2y_0 y_1 v_-(I_b) - Y_1 v_+(I_b), \\ V^{D_2} &= y_1^2 v_-(I_b) - Y_2 v_+(I_b), \end{aligned} \right\} \quad (2)$$

where  $y_0$  and  $y_1$  are the fractions of P(a) and D(a) in H(a) and  $Y_0$ ,  $Y_1$  and  $Y_2$  the fractions of  $P_2$ , PD and  $D_2$  in gaseous hydrogen, respectively.

Ethylene:

$$V^{E_l} = x_l v_-(I_a) - X_l v_+(I_a), \quad (l=0, \dots, 4), \quad (3)$$

where  $E_l$  denotes  $C_2P_{4-l}D_l$  and  $x_l$  and  $X_l$  are the fractions of  $E_l$ (a) and  $E_l$  in  $C_2H_4$ (a) and gaseous  $C_2H_4$ , respectively; H denotes hydrogen atom irrespective of P or D.

Ethane:

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

where  $A_n$  denotes  $n$ -fold deuterio-substituted ethane  $C_2P_{6-n}D_n$  and  $z_n$  is the fraction of  $n$ -fold deuterio-substituted absorbed ethyl  $C_2P_{5-n}D_n$ (a) in  $C_2H_5$ (a) ( $z_n=0$  when  $n<0$  and  $n>5$ ) and  $W_n$  the fraction of  $A_n$  in gaseous  $C_2H_6$ . The rate  $v_-(III)$  is practically zero as ethane is never adsorbed in a course of ethylene hydrogenation on metallic catalysts.

### 2-2. Analysis of steady reaction.

Steady state condition with respect to the intermediate  $C_2P_{5-n}D_n$ (a) is given as

$$(y_1 x_{n-1} + y_0 x_n) v_+(II) - z_n v_-(II) - z_n v_+(III) = 0, \quad (n=0, \dots, 5), \quad (5)$$

where  $x_n=0$  when  $n<0$  or  $n>4$ . With respect to the deuterium contents of H(a) and  $C_2H_4$ (a) we have similarly

$$(2Y_2 + Y_1) v_+(I_b) - 2y_1 v_-(I_b) - y_1 v_+(II) + \frac{2x + y_1}{3} v_-(II) - y_1 v_+(III) = 0 \quad (6)$$

and

$$4X v_+(I_a) - 4x v_-(I_a) - 4x v_+(II) + \left( \frac{2}{3} y_1 + \frac{10}{3} x \right) v_-(II) = 0, \quad (7)$$

respectively, where  $x \equiv \sum l x_l / 4$  and  $X \equiv \sum l X_l / 4$  are the D atomic fractions of  $C_2H_4$ (a) and gaseous  $C_2H_4$ , respectively.

The rate  $V_s$  of steady hydrogenation of ethylene caused by scheme (1) is expressed as

$$V_s = v_+(s) - v_-(s), \quad (s = I_a, I_b, II \text{ or } III). \quad (8)$$

From Eqs. (5), (6), (7) and (8) we have

$$y_1 x_{n-1} + y_0 x_n = z_n, \quad (9)$$

$$3(2Y_2 + Y_1 - 2y_1)v_+(I_b) + 2(x - y_1)v_-(II) = 0, \quad (10)$$

$$6(X - x)v_+(I_a) - (x - y_1)v_-(II) = 0. \quad (11)$$

In Eqs. (10) and (11),  $X$ ,  $Y_1$  and  $Y_2$  are observable, and hence the ratios of  $v_-(II)$  to  $v_+(I_a)$  and  $v_+(I_b)$  can be given as functions of  $y_1$  and  $x$ , which can be evaluated as follows.

### 2-3. Evaluation of $y_1$ , $x$ and rates of steps

When reaction is carried out with a mixture of  $C_2P_4$  and  $D_2$ , its initial condition is given by

$$X_0 = 1, \quad X_1 = X_2 = X_3 = X_4 = 0, \quad X = 0 \quad (12)$$

and

$$Y_0 = 0, \quad Y_2 = 1 - Y_1. \quad (13)$$

Substituting  $Y_0$  and  $Y_2$  of Eqs. (13) into Eqs. (2) and eliminating  $v_+(I_b)$  and  $v_-(I_b)$ , we have

$$V^{P_2} Y_1 \phi^2 - 2V^{P_2} (1 - Y_1) \phi + V^{PD} - (V^{PD} + V^{D_2}) Y_1 = 0 \quad (14)$$

or

$$\dot{Y}_0 Y_1 \phi^2 - 2\dot{Y}_0 (1 - Y_1) \phi + \dot{Y}_1 + \dot{Y}_0 Y_1 = 0, \quad (15)$$

where  $\phi \equiv y_1/y_0$  ( $= y_1/(1 - y_1)$ ),  $\dot{Y}_0 \equiv dY_0/dt$  and  $\dot{Y}_1 \equiv dY_1/dt$ . The value of  $y_1$  can be estimated by introducing the observed values of  $V^{P_2-mD_2}$  (or  $\dot{Y}_0$  and  $\dot{Y}_1$ ) into Eq. (14) or (15).

Eliminating  $z_n$ 's from Eq. (4) by the use of Eq. (9), we have

$$V^{A_n} = (y_1^2 x_{n-2} + 2y_0 y_1 x_{n-1} + y_0^2 x_n) v_+(III) \quad (16)$$

and hence

$$x_0 = V^{A_0}/y_0^2 v_+(III) = V^{A_0}/y_0^2 V_s. \quad (17)$$

Equation (3) is rewritten according to Eqs. (12) as

$$V^{E_l} = x_l v_-(I_a), \quad (l > 1), \quad (18)$$

which gives that

$$x_1 : x_2 : x_3 : x_4 = V^{E_1} : V^{E_2} : V^{E_3} : V^{E_4}. \quad (19)$$

Taking  $\sum x_i = 1$  into account, we can evaluate  $x$  ( $\equiv \sum l x_l / 4$ ) according to Eqs. (17) and (19) by introducing the observed values of  $V^{A_0}$  and  $V^{E_l}$ 's. The

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rates of respective steps of scheme (1) are evaluated finally according to Eqs. (2), (18), (10) and (8).

### 3. Experimental

A conventional, closed circulation system of *ca.* 500 cc volume used in the previous work<sup>7)</sup> was complemented with a gas pipette of *ca.* 1 cc volume into which a part of reacting gas was sampled for mass spectrometric analysis. The whole apparatus can be evacuated as low as  $1 \times 10^{-7}$  mmHg.

Catalyst was a copper film evaporated under a vacuum of  $4 \times 10^{-7}$  mmHg from a wire of 0.5 mm in diameter and with 99.9% purity. Prior to evaporation the reaction vessel in which the wire was sealed was evacuated at 500°C and the wire was electrically red-heated with a current of *ca.* 7A in *ca.* 40 mmHg hydrogen for an hour or more and degassed *in vacuo* with a current of *ca.* 5 A. The wire was then evaporated onto the inner surface of the reaction vessel immersed in an oil bath at 200°C by rising the current to 5.8 A. The geometrical area of the evaporated film was *ca.* 47 cm<sup>2</sup>.

A freshly evaporated film is signified by F. Catalytic activity of the film was satisfactorily reproducible on film R, *i. e.*, a film heated in *ca.* 20 mmHg hydrogen for 10 hrs or more and outgassed *in vacuo* for *ca.* 2 hrs both at 200°C before each run of the reaction.

Hydrogen and ethylene were purified by a conventional method as described in the previous paper<sup>7)</sup> and found to be mass spectrometrically pure. Heavy ethylene (C<sub>2</sub>D<sub>4</sub>) was prepared by deuteration of C<sub>2</sub>D<sub>2</sub> catalyzed by Pt-asbestos. Heavy acetylene (C<sub>2</sub>D<sub>2</sub>) was obtained by a reaction of heavy water (99.9 D%) with preliminarily well degassed calcium carbide. Heavy ethylene thus prepared included a little amounts of ethane and acetylene and was purified by a differential desorption from silica-gel at temperature from -100 to -45°C. Heavy ethylene thus obtained was quite free from acetylene but was still contaminated by ethane less than 0.5% and its deuterium content was *ca.* 99%.

Reaction was started by admitting an equimolar mixture of hydrogen and ethylene into the reaction vessel at 40 mmHg total pressure. The gas mixture was circulated at a rate of *ca.* 100 cc/sec and total pressure was followed by a Hg-manometer and reacting gas was sampled at times. Products other than ethane were not observed.

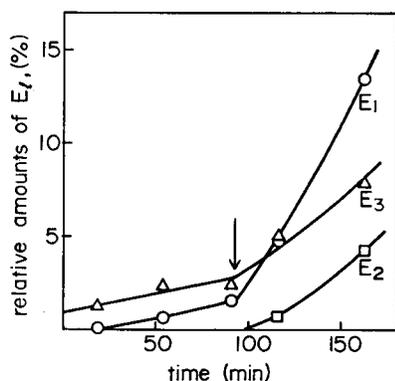
Deuterium distributions in sampled hydrogen, ethylene and ethane were determined as follows. Sampled gas was introduced into mass spectrometer

through a liquid nitrogen trap and peaks of  $m/e=2, 3$  and  $4$  were registered at  $70$  V of ionization voltage. Hydrocarbon in the trap was then evaporated and its mass spectrum ( $m/e$  from  $28$  to  $32$ ) was registered with an ionization voltage as low as the spectrum to be consisted exclusively of the parent peak of ethylene. The hydrocarbon was collected again into the liquid nitrogen trap and analyzed by gaschromatography-mass spectrometer. Ethane was separated from ethylene by silica-gel column at room temperature and its mass spectrum was registered at  $70$  V.

Relative amounts of  $P_2$ ,  $PD$  and  $D_2$  were evaluated from the relative heights of peaks of  $m/e=2, 3$  and  $4$ . Heights of these peaks were corrected with regards the difference of focus of these ion beams and the contribution of  $D^+$  ions formed from  $D_2$  to the peak of  $m/e=2$ , by referring to the mass spectra of an equilibrated mixture of  $P_2$  and  $D_2$  with known D atomic fraction and  $D_2$ .

Relative amounts of ethylenes  $E_i$ 's were estimated directly by the relative heights of peaks of  $m/e$  from  $28$  to  $32$  with a correction of the natural abundance of  $^{13}C$ .

Relative amounts of ethanes  $A_n$ 's were derived as usual<sup>8)</sup> from mass spectra of respective deuterated ethanes calculated from observed mass spectrum of  $C_2P_6$  by neglecting of the isotopic effect on the fragmentation of ions in mass spectrometer. Observation of the relative amounts of  $A_n$ 's are thus inaccurate as compared with the cases of hydrogen and ethylene.



**Fig. 1.** Deuterium distribution in ethylene formed by the hydrogen exchange reaction between  $C_2P_4$  and  $C_2D_4$  on evaporated Cu film R at  $119^\circ C$ : an arrow indicates the addition of hydrogen.

#### 4. Results of experiments

Figure 1 shows the result of hydrogen exchange reaction between  $14.4$  mmHg  $C_2P_4$  and  $5.2$  mmHg  $C_2D_4$  on film R. Hydrogen of  $0.6$  mmHg was added at the time indicated by an arrow in the figure. The acceleration of exchange by this addition of hydrogen suggests that the exchange between  $C_2P_4$  and  $C_2D_4$  proceeds *via* a half-hydrogenated state of adsorbed ethylene. A slight exchange caused before the addition of hydrogen might be due to a little amount of adsorbed hydrogen atoms remained by preliminar reduction

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and outgassing of the film.

Table 1 shows the result of  $P_2$ - $D_2$  equilibration reaction observed with films F, R and S, where S is a film F once used for the hydrogenation and outgassed *in vacuo* at the reaction temperature. The equilibration proceeded

TABLE 1.  $P_2$ - $D_2$  equilibration on evaporated Cu films at 9 mmHg and 119°C.

Sorts of film	time (hr)	$P_2$	PD	$D_2$ (%)
F	0	47.0	2.5	50.6
	20.17	24.8	49.2	26.1
S	1.17	44.8	6.2	49.6
	2.10	43.9	8.7	47.4
	20.75	31.6	31.6	31.4
R	1.20	44.1	5.5	50.5
	4.00	4.60	12.9	41.4

slowly and evolution rate of PD was the same order of magnitude of the rate of ethylene hydrogenation on the same film. Catalytic activity order of these films for the equilibration was  $F > S \cong R$ , while catalytic activity of film R for ethylene hydrogenation was close to that of film F and *ca.* 1/500 of that of an evaporated nickel film R.

On the basis of the above results it may be concluded that in a steady hydrogenation, ethylene is associatively, while hydrogen is dissociatively, adsorbed on copper to form an adsorbed ethyl. Accordingly, ethylene hydrogenation on copper is concluded to proceed by scheme (1).

TABLE 2. Rates of hydrogenation and evolution of deuterio-substituted isomers of hydrogen, ethylene and ethane at the initial stage of reaction with an equimolar mixture of deuterium and light ethylene. Initial total pressure was 40 mmHg.

Temp. (°C)	$V_s$ (mmHg/hr)	Hydrogen (%/hr)		Ethylene (%/hr)		Ethane (%/hr)
		$Y_0$	$Y_1$	$\dot{X}_1$	$\dot{X}_2$	
103	0.22	1.125	0.263	3.60	0.16	71.5
78	0.10	0.362	0.125	1.10	—	71.0
135	0.50	6.200	1.270	13.8	1.00	55.6
19	0.20	0.960	0.260	3.30	0.22	67.0

For measurement of the initial distributions of deuterio-substituted products, the reaction of  $C_2P_4$  with  $D_2$  was arranged to proceed less than 10%. Initial evolution rates of the deuterated isomers were estimated from the inclination of initial time courses of these products. The results obtained are shown in Table 2. It was found that evolution of  $P_2$  is several times faster than that of PD and  $C_2P_6$  is predominantly formed.

The D atomic fraction  $y_1$  of H(a), fraction  $x_i$  of  $E_i$ (a) and D content  $x$  of  $C_2H_4$ (a) are estimated as given in Table 3 from the results of Table 2. The values of  $y_1$  and  $x$  are very small and the former decreases with rise of reaction temperature, while the latter increases.

Unidirectional rates of steps of scheme (1) are evaluated as given in

TABLE 3. Values of  $y_1$ ,  $x_i$  and  $x$

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

Table 4 and ARRHENIUS plots of these rates are given in Fig. 2. We see that steps  $I_a$  and II are far faster than the others and  $v_-(I_b)$  becomes far larger than  $v_+(III)$ , getting close to  $v_+(I_b)$  with rise of reaction temperature. Evaluation of  $v_-(I_a)$  and  $v_-(II)$  is inaccurate owing to large errors of evalua-

TABLE 4. Calculated unidirectional rates of the elementary steps (mmHg/hr).

Temp. (°C)	$v_+(I_b)$	$v_-(I_b)$	$v_+(I_a)$	$v_+(II)$	$v_+(III)$
103	0.495	0.275	6.71	20.0	0.22
78	0.199	0.099	7.47	3.81	0.10
135	1.99	1.49	9.40	$\infty$	0.50
91	0.446	0.246	7.54	13.7	0.20

tions of  $x_i$  and  $x$ , which are caused by the value of  $x_0$  evaluated by Eq. (17) with the amount of  $A_0$  accompanying large error. Steps  $I_a$  and II are far faster than the others as seen from the very rapid evolution of deuterio-ethylene.

In connection with this conclusion, the reaction with a mixture of equimolar  $C_2P_4$ ,  $C_2D_4$ ,  $P_2$  and  $D_2$  was carried out, and the results are given in

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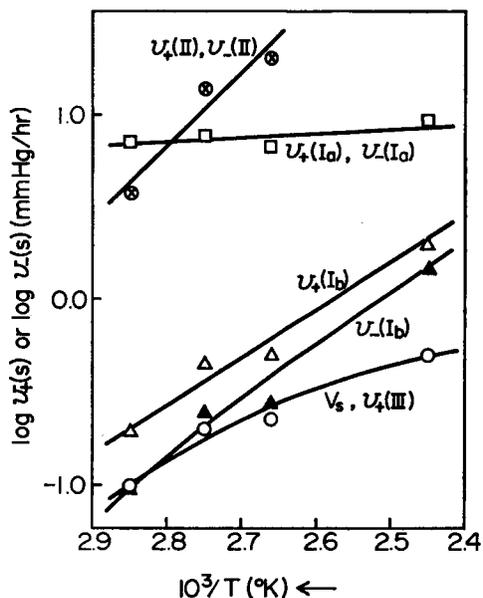


Fig. 2. ARRHENIUS plots of the rates of elementary steps.

Table 5. Both at 92 and 126°C hydrogen exchange between  $C_2P_4$  and  $C_2D_4$  was nearly equilibrated, whereas ethylene hydrogenation and  $P_2$ - $D_2$  equilibration reaction were far from their equilibria.

TABLE 5. Hydrogen exchange in course of reaction with a mixture ( $P_2$  24.1%,  $D_2$  26.3%,  $C_2P_4$  24.8% and  $C_2D_4$  24.8%) over evaporated Cu film R.

Temp. (°C)	Time (hr)	Conversion (%)	Hydrogen (%)			Ethylene (%)				
			$P_2$	PD	$D_2$	$E_0$	$E_1$	$E_2$	$E_3$	$E_4$
92	8	5.9	46.9	4.4	48.7	6.8	25.4	36.9	24.6	6.4
	32	11.8	44.7	7.3	48.0	7.2	26.4	36.9	23.8	5.7
126	1.7	7.4	44.6	6.9	48.5	7.3	25.5	36.4	24.0	6.8
	3.5	14.3	42.1	10.6	47.3	6.5	25.1	36.9	24.8	6.7
	21.3	47.8	33.4	29.4	37.2	5.0	22.3	36.8	27.7	8.3

## 5. Discussion

Tables 4 and 5 show that steps  $I_a$  and II are reversible and remarkably faster than steps  $I_b$  and III, that is, the rate of ethylene hydrogenation over copper catalyst is controlled mainly by step  $I_b$  or III, and also that the

ratio of  $v_+(I_b)$  to  $v_-(I_b)$  becomes smaller with rise of reaction temperature, suggesting that step  $I_b$  is getting near to its equilibrium, and hence the rate-determining step shifts from  $I_b$  to III. Such a characteristic of the reaction mechanism of present hydrogenation can be elucidated more distinctly by the analysis of the reaction structure theory developed by HORIUTI<sup>9</sup>.

The theory expresses unidirectional rates of respective steps of scheme (1) as

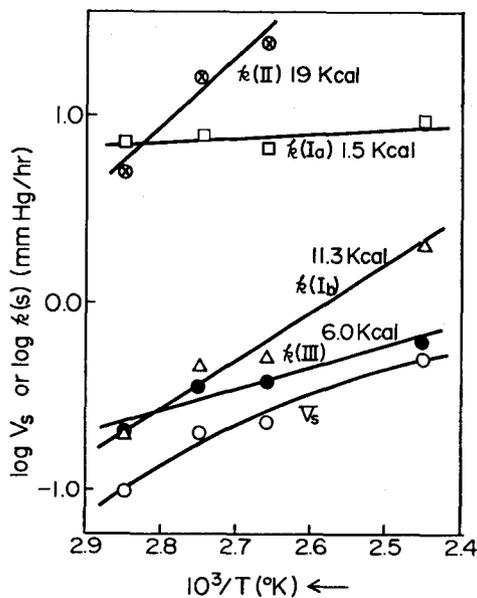
$$\left. \begin{aligned} v_+(I_a) &= k(I_a), & v_-(I_a) &= k(I_a)\gamma(E), \\ v_+(I_b) &= k(I_b), & v_-(I_b) &= k(I_b)\gamma(H)^2, \\ v_+(II) &= k(II)\gamma(H)\gamma(E), & v_-(II) &= k(II)\gamma(\varepsilon), \\ v_+(III) &= k(III)\gamma(H)\gamma(\varepsilon), \end{aligned} \right\} \quad (20)$$

where  $\gamma(E)$ ,  $\gamma(H)$  or  $\gamma(\varepsilon)$  is the activity of adsorbed  $C_2H_4$ ,  $H$  or  $C_2H_5$  each referred to gaseous  $C_2H_4$ ,  $1/2 \cdot H_2$  or the mixture of  $C_2H_4 + 1/2 \cdot H_2$ , respectively, and  $k(s)$  ( $s = I_a, I_b, II$  or  $III$ ) is the forward unidirectional rate of step  $s$  in a special case where all of the steps of scheme (1) other than  $s$  are in equilibria. According to the theory, the smallest one among  $k(I_a)$  etc. gives the upper bound of the steady hydrogenation rate  $V_s$ . Thus, in a typical case with nickel catalyst<sup>4</sup> where  $k(I_b)$  and  $k(III)$  are far smaller than  $k(I_a)$  and  $k(II)$  in the observed temperature range and  $k(I_b)$  becomes larger than  $k(III)$  with rise of reaction temperature, we see that ethylene hydrogenation is rate-determined by step  $I_b$  at lower temperatures and by step III at temperatures higher than the optimum one where  $k(I_b)$  equals to  $k(III)$ . Such changes of the relative magnitude of  $k(s)$ 's with reaction temperature are called the reaction structure.

The reaction structure of the present case was derived as shown in Fig. 3 according to Eqs. (20) with the result of Table 4; the annexed values in Fig. 3 are activation heats of respective steps. We see that with monotoneous increase of  $V_s$  the slowest step shifts at *ca.* 80°C from  $I_b$  to III; activation heat of the latter step is positive in contrast with the case of nickel catalyst<sup>4</sup> with a negative activation heat of step III.

Kinetics of ethylene hydrogenation ever observed with copper catalyst are investigated with reference to the reaction structure derived above. Activation heats of the hydrogenation observed by GRASSI<sup>10</sup> and PEASE<sup>11</sup> with powdered copper catalysts are given in Table 6. The decrease of activation heat with rise of reaction temperature coincides with the present result. Pressure dependences ever observed on hydrogenation rate  $V_s$  have diverged widely; however, most of them show that  $V_s$  is nearly first order

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Fig. 3. ARRHENIUS plots of  $k(s)$ 's.TABLE 6. Activation heats of ethylene hydrogenation on Cu powder observed by GRASSI<sup>10)</sup> and PEASE<sup>11)</sup>

	150-200°C	200-250°C	250-275°C
GRASSI	12.0	1.3	0
PEASE	10.8	7	—

with hydrogen partial pressure. PEASE and HARRIS<sup>12)</sup> have observed that the order of reaction with ethylene partial pressure changes from zero at 100°C to unity at 220°C. These results support the present conclusion that  $V_s$  is controlled by step  $I_b$  or III, respectively, at low or high reaction temperature range.

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