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REACTION STRUCTURE OF ETHYLENE HYDROGENATION ON METALLIC CATALYSTS

Part 3. The Reaction on Evaporated Platinum and Rhodium Films

By

Shinri SATO and Koshiro MIYAHARA^{*)}

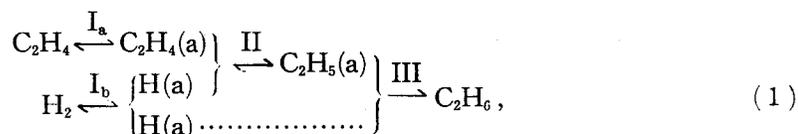
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Abstract

Hydrogenation of ethylene on evaporated Pt and Rh films was investigated at temperatures from -45 to 85°C with deuterium as a tracer. Mass spectrometric analysis of produced deuterio-ethanes was made more accurate by the method of least squares and the rates of elementary reactions were evaluated similarly to the previous work. It was found with both metals that chemisorption of hydrogen rate-determines the hydrogenation and adsorption of ethylene is slow and nearly irreversible. Activity order of various metals for ethylene hydrogenation was discussed with reference to the relative rates of elementary steps and interpreted in terms of the rate of hydrogen chemisorption retarded by strongly adsorbed ethylene.

Introduction

In the previous works^{1,2)} steady hydrogenation of ethylene was investigated with evaporated Cu and Ni films and deuterium as a tracer, and the following mechanism was concluded:



where a rate-determining step is I_b or III at temperatures sufficiently below or above *ca.* 100°C , respectively. Step I_b on Ni film²⁾ was proposed to be composed of two elementary steps, *i.e.*, dissociative adsorption of hydrogen and change of state or surface diffusion of adsorbed hydrogen atoms. It

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was found from the rates of elementary steps of scheme (1) evaluated according to the reaction structure theory^{3,4)} that the activation heat of step III was positive with Cu film¹⁾ but negative with Ni film²⁾ and the ratio of the rate of step I_a to the rate of steady hydrogenation on Ni film²⁾ was far smaller than that on Cu film.¹⁾

In the present work the same method of analysis is applied to ethylene hydrogenation on evaporated Pt and Rh films which are known^{4,5)} to be highly active for olefin hydrogenation among transition metals. Discussions are given on the activity order of transition metals for ethylene hydrogenation with reference to the rate of hydrogen chemisorption retarded by strongly adsorbed ethylene.

Experimental

Evaporated films of Pt and Rh were prepared as follows. A wire of Pt (0.4 mm ϕ \times 15 cm) or Rh (0.24 mm ϕ \times 15 cm) of 99.9% purity was sealed in a cylindrical reactor of a conventional, closed circulation system (*ca.* 600 cc) and the reactor was evacuated at 500°C. Platinum wire was electrically red-heated in hydrogen, outgassed well in a vacuum of 3×10^{-7} mmHg with a current of *ca.* 5 A and then evaporated with 6.3 A onto the inner surface of reactor kept at 200°C. Rhodium film was prepared similarly; outgassed with *ca.* 1.4 A and evaporated with 1.9 A onto the reactor wall kept at 300°C. The geometrical surface area of these films was *ca.* 9 cm². Catalytic activity of the films at an early stage of ethylene hydrogenation was satisfactorily reproducible by preliminary heating in *ca.* 20 mmHg hydrogen for 10 hr or more followed by evacuation for *ca.* 2 hr at 200°C (Pt film) or 300°C (Rh film).

Ethylene of 90 ¹³C atom % was obtained from Prochem./BOC Ltd. and was purified as usual.¹⁾

Ethane produced by ethylene deuteration on Pt or Rh is much deuterio-substituted and, accordingly, the measurement of its deuterium distribution is inevitably inaccurate by the usual mass-spectrometric analysis¹⁾, even if isotopic effect⁶⁾ on fragmentation of deuterio-ethane in a mass-spectrometer is taken into account. In the present work, mass spectrum of deuterio-ethane was analyzed by the following least square calculation. The relative amount, Z_n , of n -fold deuterio-substituted ethane is given as a solution of the following equations.

$$\sum_{n=0}^6 C_n^m Z_n = M_m, \quad (m=28, 29, \dots, 36). \quad (2)$$

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The coefficient C_n^m is a relative height of peak at mass number n referred to the peak height of parent ion in a theoretical⁶⁾ mass spectrum of n -fold deuterio-substituted ethane and M_m is the same in an observed mass spectrum of deuterio-ethane sample. The values of Z_n 's were calculated according to Eqs. (2) by applying the method of least squares, and the result was sufficiently convergent.

All other experimental procedures and materials used were the same as described in the previous papers.^{1,2)}

Evaluation of Unidirectional Rates of Elementary Steps

Relative rates of steps of scheme (1) are evaluated according to the previous method,^{1,2)} which is summarized in the followings. Symbols used are :

- 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),
 V^{E_l} : evolution rate of l -fold deuterio-substituted ethylene, E_l ,
 $V^{P_{2-m}D_m}$: evolution rate of m -fold deuterio-substituted hydrogen, $P_{2-m}D_m$,
 V^{A_n} : evolution rate of n -fold deuterio-substituted ethane, A_n ,
 X_l, x_l : fraction of E_l in gaseous ethylene or of $E_l(a)$ in adsorbed ethylene ,
 Y_m : fraction of $P_{2-m}D_m$ in gaseous hydrogen ,
 X, x : deuterium fraction of gaseous ethylene ($\equiv \sum l X_l / 4$) or adsorbed ethylene ($\equiv \sum l x_l / 4$),
 y_1, y_0 : fraction of D(a) or P(a) in H(a) ($y_1 + y_0 = 1$),
 ϕ : $\equiv y_1 / y_0$.

Evolution rates of deuterio-substituted ethylene, hydrogen and ethane during steady hydrogenation of ethylene are given according to scheme (1) as

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

$$V^{P_{2-m}D_m} = \frac{2}{(2-m)! m!} y_0^{2-m} y_1^m v_-(I_b) - Y_m v_+(I_b), \quad (m=0, 1, 2) \quad (4)$$

and

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$$V^{A_n} = (y_0^2 x_n + 2 y_0 y_1 x_{n-1} + y_1^2 x_{n-2}) v_+(\text{III}), \quad (n=0, \dots, 6) \quad (5)$$

respectively, where isotopic effect is ignored and the term including $v_-(\text{III})$ is neglected in Eq. (5) since step III of scheme (1) is perfectly irreversible.⁴⁾ Steady state conditions for the amounts of adsorbed intermediates and the deuterium fraction of adsorbed ethylene are expressed, respectively, as

$$V_s = v_+(s) - v_-(s), \quad (s = \text{I}_a, \text{I}_b, \text{II or III}) \quad (6)$$

and

$$6(X-x) v_+(\text{I}_a) - (x-y_1) v_-(\text{II}) = 0. \quad (7)$$

Using the initial condition of reaction with C_2P_4 and D_2 , $X_l (l > 1) = X = Y_0 = Y_1 = 0$, we can rewrite Eqs. (3), (4) and (7) as

$$v_-(\text{I}_a) = \Sigma l V^{E_l} / 4x = V^{E_l} / x_l, \quad (l > 1), \quad (8)$$

$$v_-(\text{I}_b) = \left(V^{P_2} + \frac{1}{2} V^{PD} \right) / (1-y_1) \quad (9)$$

and

$$v_-(\text{II}) = 6xv_+(\text{I}_a) / (y_1 - x), \quad (10)$$

respectively. The forward unidirectional rates $v_+(s)$'s ($s = \text{I}_a, \text{I}_b, \text{II}$ and III) are given by Eqs. (6), (8), (9) and (10). In above mentioned equations, the evolution rates V^{E_l} 's *etc.* are measurable and hence the unidirectional rates of steps are given as functions of y_1 and x . The value of y_1 is given according to the equation,

$$Y_1 \phi^2 - 2 Y_2 \phi + \frac{V^{PD}}{V^{P_2}} Y_2 - \frac{V^{D_2}}{V^{P_2}} Y_1 = 0 \quad (11)$$

or

$$3\phi^2 + 2 \left(\frac{V^{E_2}}{V^{E_1}} - \frac{V^{A_1}}{V^{A_0}} \right) \phi + \frac{V^{A_2}}{V^{A_0}} - \frac{V^{A_1}}{V^{A_0}} \frac{V^{E_2}}{V^{E_1}} = 0, \quad (12)$$

by measuring Y_m *etc.* The values of x_l 's are then calculated from the simultaneous equations,

$$\left. \begin{aligned} \Sigma x_l &= 1, \\ x_1 &= (V^{A_1} / V^{A_0} - 2\phi) x_0, \\ x_l &= V^{E_l} x_1 / V^{E_1}, \quad (l=2, 3, 4) \end{aligned} \right\} \quad (13)$$

and, accordingly, $x (\equiv \Sigma l x_l / 4)$ can be evaluated.

Results

Platinum Film

Platinum film evaporated at room temperature was *ca.* 10 times more active for ethylene hydrogenation than the one evaporated at 200°C and was markedly deactivated by the pretreatment with hydrogen at 200°C, indicating considerable sintering of the film at 200°C. The film evaporated at 200°C was slightly less active than Ni film evaporated at 300°C with a roughness factor of *ca.* 3.⁷⁾

Reaction of C₂P₄ with D₂. Reaction was carried out at temperatures from 36 to 85°C with equimolar C₂P₄ and D₂ and the reacting gas sampled at times was subjected to mass-spectrometric analysis.¹⁾ Appreciable amounts of deuterio-ethylene and PD were observed exceptionally at the initial stage of reaction at 85°C, possibly owing to dissociative adsorption of ethylene. These unsteady evolutions were corrected in the evaluation of steady rates. Deuterium distribution in ethane was practically unchanged during the reaction.

Table 1 shows the initial rates of hydrogenation and evolutions of

TABLE 1. Rates of hydrogenation and evolutions of deuterio-substituted hydrogen, ethylene and ethane at the initial stage of reaction with equimolar C₂P₄ and D₂ on Pt film: Initial total pressure, 40 mmHg.

Temp. (°C)	Hydrogenation V_s (mmHg/min)	Hydrogen (%/min)		Ethylene (%/min)				Ethane ^{*)} (%)		
		P ₂	PD	E ₁	E ₂	E ₃	E ₄	A ₀	A ₁	A ₂
36	0.17	0.006	0.04	0.13	0.03	0.01	0.003	19.6	34.7	25.1
53	0.42	0.03	0.02	0.45	0.10	0.03	0.006	18.5	36.5	25.7
69	0.60	0.04	0.27	0.55	0.16	0.05	0.01	21.9	34.7	20.9
85	1.20	0.17	0.98	1.48	0.40	0.15	0.05	18.0	32.5	25.0

*) Value of V_{A_n}/V_s

TABLE 2. Values of y_1 , x_i 's and x (Pt film)

Temp. (°C)	y_1 (H)	y_1 (A)	x_0	x_1	x_2	x_3	x_4	x
36	0.77	0.34	0.45	0.41	0.10	0.03	0.01	0.19
53	0.81	0.42	0.55	0.34	0.08	0.02	0.0	0.15
69	0.78	0.36	0.54	0.33	0.10	0.03	0.01	0.16
85	0.74	0.34	0.41	0.42	0.11	0.04	0.01	0.21

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TABLE 3. Unidirectional rates of elementary steps
(mmHg/min) (Pt film)

Temp. (°C)	$v_+(I_b)$	$v_-(I_b)$	$v_+(I_a)$	$v_-(I_a)$	$v_+(II)$	$v_+(III)(=V_s)$
36	0.18	0.008	0.23	0.06	1.9	0.17
53	0.47	0.05	0.68	0.26	2.5	0.42
69	0.66	0.06	0.94	0.34	5.0	0.60
85	1.40	0.20	1.91	0.71	19.0	1.20

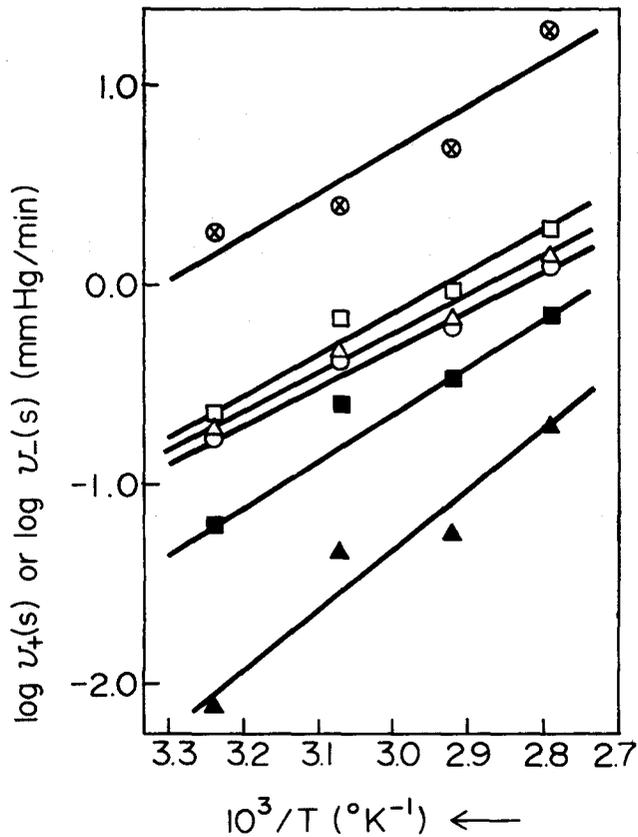


Fig. 1. Arrhenius plots of the rates of elementary steps constituting ethylene hydrogenation on Pt film at 20 mmHg of partial pressures of ethylene and deuterium:

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

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deutero-substituted hydrogen, ethylene and ethane. Evolutions of P₂, PD and deutero-ethylenes were far slower than hydrogenation, and monodeutero-ethane, A₁, was a principal product in contrast with the cases of Cu¹⁾ and Ni²⁾ catalysts where light ethane was predominantly formed at an early stage of reaction. Values of y_1 , x_i 's and x were obtained from the results of Table 1 as given in Table 2, where $y_1(\text{H})$ or $y_1(\text{A})$ is the value of y_1 calculated according to Eq. (11) or (12), respectively. We see that $y_1(\text{H})$ is larger than $y_1(\text{A})$, similarly to the case of Ni catalyst.²⁾ Excess of $y_1(\text{H})$ over $y_1(\text{A})$ is probably due to a side reaction giving rise to PD formation as discussed previously,²⁾ and, accordingly, the values of x_i 's and x in Table 2 were calculated from $y_1(\text{A})$. Rates of steps were evaluated as given in Table 3 and Arrhenius plots of these rates are shown in Fig. 1. Steps I_a and I_b are far slower than step II and the activation heat of ethylene hydrogenation is 8.4 kcal/mole.

Reaction with a mixture of C₂P₄, C₂D₄, P₂ and D₂. In order to make sure the above conclusion, reaction with equimolar C₂P₄, C₂D₄, P₂ and D₂ was carried out at temperatures from 33 to 82°C: the results are given in Table 4, Figs. 2 a) and b). Hydrogen mixings between C₂P₄ and C₂D₄ and between P₂ and D₂ are very slow in conformity with the above conclusion of slow steps I_a and I_b. A marked decrease of P₂ as compared with D₂ is due to isotopic effect and its magnitude α (Table 4) is nearly equal to those observed with Cu¹⁾ and Ni²⁾ films. Figure 3 shows that the present hydrogenation with a mixture of P₂ and D₂ is *ca.* 1.3 times faster than deuteration of C₂P₄.

TABLE 4. Rates of hydrogen mixings in hydrogen and ethylene at the initial stage of reaction with equimolar C₂P₄, C₂D₄, P₂ and D₂ on Pt film: Initial total pressure, 40 mmHg.

Temp. (°C)	Hydrogen (%/min)			Ethylene (%/min)		α^*	$2V^{\text{PD}}/V_{\text{s}}$
	P ₂	PD	D ₂	E ₁	E ₂		
33	-0.4	0.3	0	0.05	0.02	2.1	0.60
53	-0.7	0.6	0	0.12	0.06	1.7	0.48
69	-1.4	1.7	0	0.37	0.16	2.0	0.76
82	-1.9	2.8	0	0.62	0.27	2.0	0.84

*) $\alpha \equiv V^{\text{P}}/V^{\text{D}}$, *i. e.*, a ratio of decreasing rate of P to that of D in hydrogen gas.

Adsorption of a mixture of C₂P₄ and C₂D₄. Adsorption of 3:1 mixture of C₂P₄ and C₂D₄ was carried out at 19 mmHg and 53°C. Hydrogen

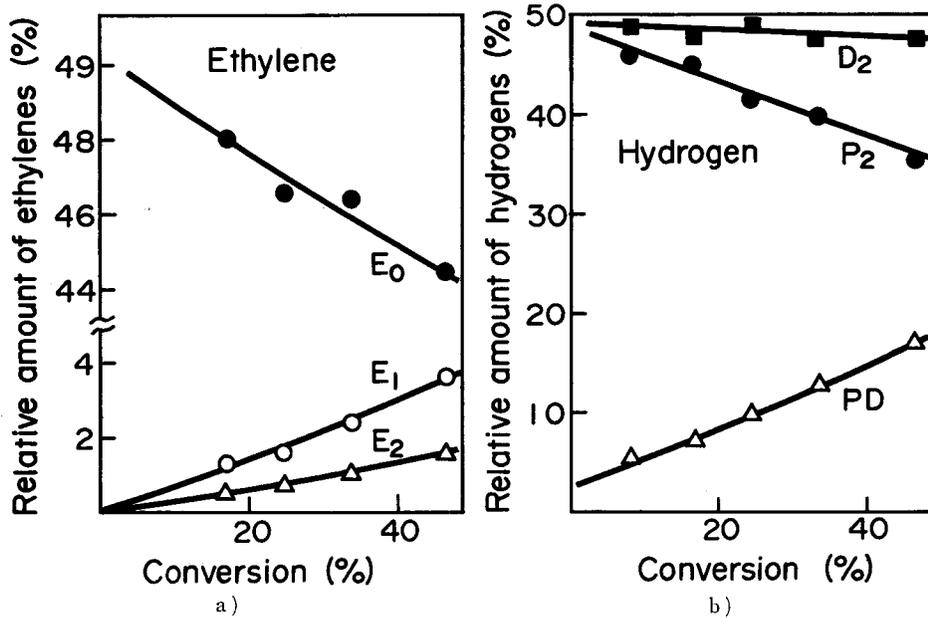


Fig. 2. Hydrogen mixings in ethylene and hydrogen during the reaction with equimolar C_2P_4 , C_2D_4 , P_2 and D_2 on Pt film at $69^\circ C$;
 a) hydrogen mixing between C_2P_4 and C_2D_4 and b) P_2 - D_2 equilibration.

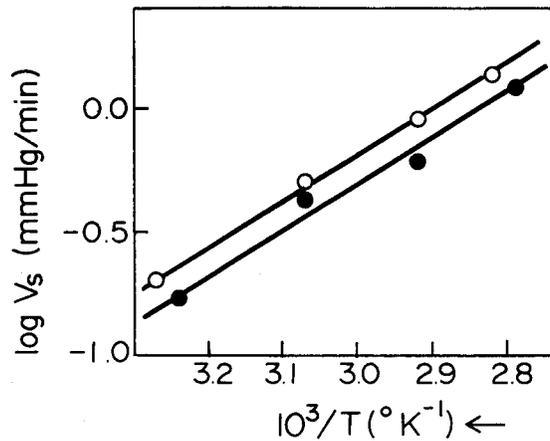


Fig. 3. Arrhenius plots of the rates of ethylene hydrogenation on Pt film; ○, the reaction with C_2P_4 , C_2D_4 , P_2 and D_2 , and ●, the reaction with C_2P_4 and D_2 .

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mixing in ethylene was not caused by 45 min contact, indicating that adsorption of ethylene on Pt film is irreversible and/or associative.

Reaction with a mixture of C₂P₄, ¹³C₂P₄ and P₂. Ethylene of 20 mmHg containing 20% ¹³C₂P₄ was hydrogenated at 70°C with 20 mmHg P₂. None of ¹³CP₂CP₂ or ¹³CP₃CP₃ was detected throughout the reaction, indicating the absence of carbon atom rearrangement as reported by MORROW.⁸⁾

P₂-D₂ equilibration. Mixture of equimolar P₂ and D₂ was brought into contact with Pt film at 10 mmHg and 16°C. The initial rate of PD formation was *ca.* 1.8 mmHg/min, from which the forward unidirectional rate of hydrogen chemisorption at 20 mmHg hydrogen was evaluated as *ca.* 7.2 mmHg/min. This value is *ca.* 300 times larger than the rate of ethylene hydrogenation at the same pressure of hydrogen.

Rhodium Film

Reaction of C₂P₄ with D₂. Catalytic activity at 0°C of Rh film for

TABLE 5. Rates of hydrogenation and evolutions of deuterio-substituted hydrogen, ethylene and ethane at the initial stage of reaction with equimolar C₂P₄ and D₂ on Rh film: Initial total pressure, 40 mmHg.

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
0	1.4	0.16	1.07	1.04	0.21	0	18.3	31.2	23.9
-45	0.15	0.0043	0.062	0.035	0.007	0	22.1	29.4	21.2

*) Value of V^{A_n}/V_s.

TABLE 6. Values of y₁, x_i's and x (Rh film)

Temp. (°C)	y ₁ (H)	y ₁ (A)	x ₀	x ₁	x ₂	x
0	0.77	0.34	0.54	0.38	0.08	0.14
-45	0.88	0.27	0.59	0.34	0.07	0.12

TABLE 7. Unidirectional rates of elementary steps
(mmHg/min) (Rh film)

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	0.021	0.95	0.15

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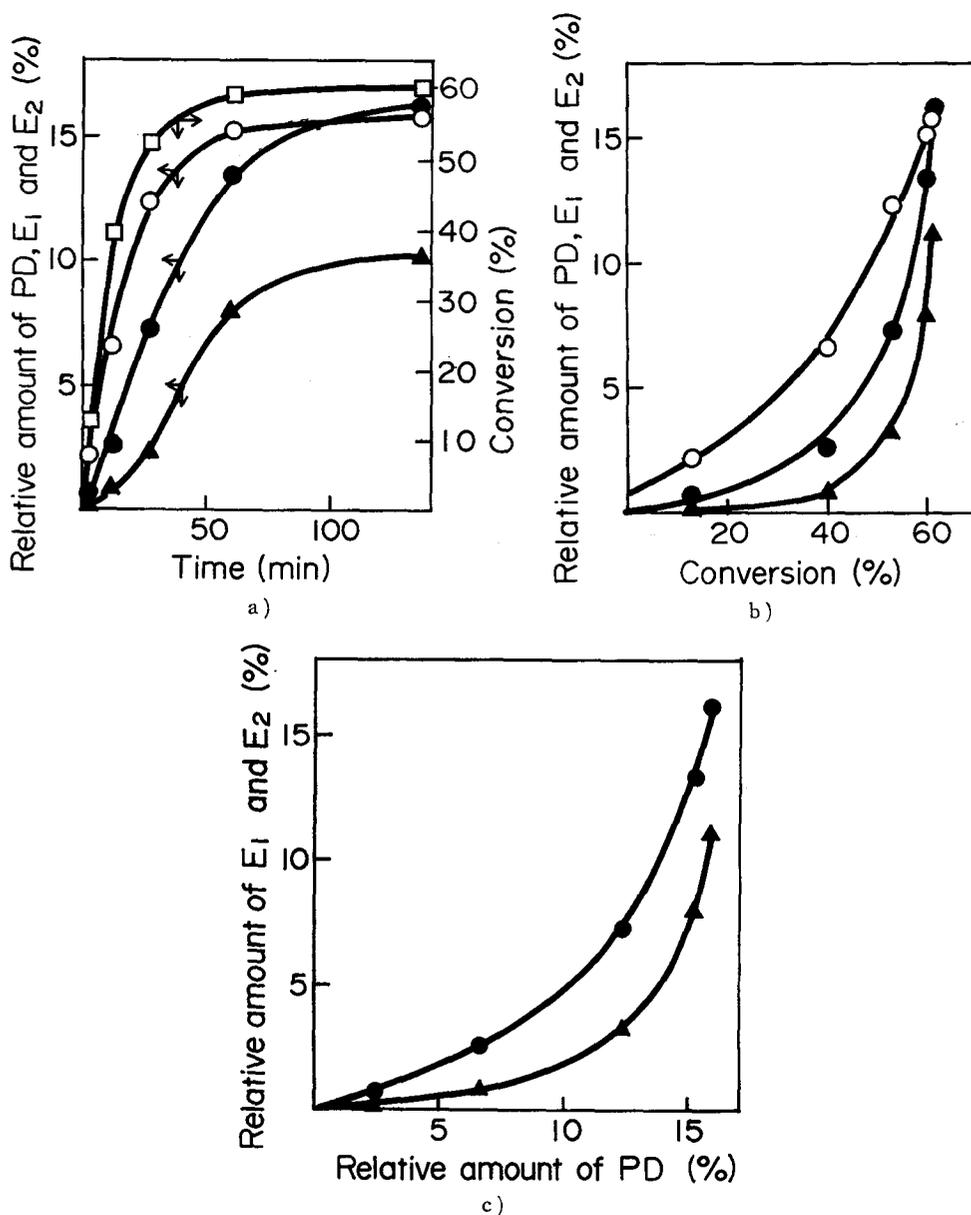


Fig. 4. Deactivation of Rh film during the reaction with C_2P_4 , C_2D_4 , P_2 and D_2 at $-13^\circ C$; a) time courses of formations of ethane, PD, E_1 and E_2 , b) formations of PD, E_1 and E_2 plotted against ethane formation, and c) formations of E_1 and E_2 plotted against PD formation.

\square , Conversion of ethylene to ethane; \circ , PD; \bullet , E_1 ; \blacktriangle , E_2 .

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ethylene hydrogenation was *ca.* 40 times higher than that of Ni film. Deuterium distributions in products of the reaction with equimolar C_2P_4 and D_2 at 0 and $-45^\circ C$ were quite similar to those observed with Pt film, indicating a common reaction mechanism. From the evolution rates of respective deuterio-substituted products given in Table 5 the values of y_1 , x_i 's and x are calculated as given in Table 6 and the rates of steps are evaluated similarly to the case of Pt film. The results (Table 7) show that steps I_a and I_b are considerably slower than step II.

Reaction with a mixture of C_2P_4 , C_2D_4 , P_2 and D_2 . Results of the reaction at 0 and $-22^\circ C$ (Table 8) are consistent with the conclusion derived just above. Value of α is somewhat smaller than that with Pt film.

TABLE 8. Rates of hydrogen mixings in hydrogen and ethylene at the initial stage of reaction with equimolar C_2P_4 , C_2D_4 , P_2 and D_2 on Rh film: Initial total pressure, 40 mmHg.

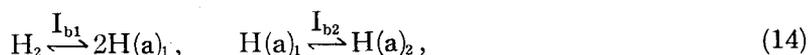
Temp. (°C)	Hydrogen (%/min)			Ethylene (%/min)		α	$2V^{PD}/V_s$
	P_2	PD	D_2	E_1	E_2		
0	-1.14	1.52	-0.42	0.92	0.48	1.2	0.32
-22	-0.22	0.35	-0.035	0.15	0.07	1.1	0.23

Rhodium film was remarkably deactivated during ethylene hydrogenation at temperatures below $0^\circ C$ and hydrogen mixings between C_2P_4 and C_2D_4 and between P_2 and D_2 were retarded as shown in Fig. 4 a). These mixings, however, were not readily retarded as compared with the hydrogenation as shown in Fig. 4 b) and the deactivation for P_2 - D_2 equilibration was more noticeable than that for hydrogen mixing in ethylene as shown in Fig. 4 c).

Similar deactivation of Pt film for the hydrogenation as well as the hydrogen mixings was observed at temperatures below $30^\circ C$.

Discussion

The difference between $y_1(H)$ and $y_1(A)$ observed with Pt and Rh films may be not due to isotopic effect, because the value of α on these films is not larger than that on Cu film¹⁾, with which this difference was not observed. In the preceding work with Ni catalyst²⁾ this difference was interpreted by step I_b of scheme (1) composed of two steps as



where $H(a)_1$ or $H(a)_2$ is an adsorbed hydrogen atom inactive or active, respectively, for hydrogenation of $C_2H_4(a)$ and $C_2H_5(a)$. Deuterium fraction of $H(a)_1$ or $H(a)_2$ during ethylene deuteration is given by $y_1(H)$ or $y_1(A)$, respectively, and, accordingly, $y_1(H)$ should exceed $y_1(A)$ when step I_{b2} is not in equilibrium. The same interpretation is applicable to the present case with reference to the following results of observations of various states of hydrogen adsorbed on Pt and Rh catalysts. PLISKIN and EISCHENS⁹⁾ and ELEY *et al.*¹⁰⁾ have concluded from their infrared spectroscopic observations two states of hydrogen atoms adsorbed on a silica-supported Pt catalyst, and PICKERING and ECKSTROM¹¹⁾ have observed with an infrared spectroscopy of reflection type as many as 23 absorption bands attributed to various states of hydrogen adsorbed on evaporated Rh film. TSUCHIYA *et al.*,¹²⁾ on the other hand, have observed four peaks of a temperature programmed desorption of hydrogen adsorbed on a Pt black catalyst and found¹³⁾ that adsorbed hydrogen giving one of the peaks can be replaced with gaseous hydrogen and this replacement is immeasurably slow at -195°C , whereas P_2 - D_2 equilibration occurs at the same temperature.

Unidirectional rates of steps I_{b1} and I_{b2} of scheme (14) are evaluated as follows. On account of the $y_1(H)$ value being *ca.* 0.5 during the reaction with equimolar C_2P_4 , C_2D_4 , P_2 and D_2 , $v_-(I_{b1})$ is approximated by $2V^{PD}$ according to Eq. (4) at early stage of the reaction, where $Y_1 \simeq 0$. Forward rate $v_+(I_{b1})$ is evaluated from $v_-(I_{b1})$ according to the steady state condition,

$$V_s = v_+(I_{b1}) - v_-(I_{b1}) = \frac{1}{2} (v_+(I_{b2}) - v_-(I_{b2})). \quad (15)$$

Forward rate of step I_{b2} is given in terms of $v_+(I_b)$ and $v_-(I_{b1})$ as²⁾

$$v_+(I_{b2}) = 2v_+(I_b) v_-(I_{b1}) / (v_+(I_{b1}) - v_+(I_b)). \quad (16)$$

With Pt film at 53°C , $v_+(I_{b2})$ is evaluated from $v_+(I_b)$ and $v_-(I_{b1}) (=2V^{PD})$ given in Tables 3 and 4 to be about twice as large as $v_+(I_{b1})$, indicating step I_b being rate-controlled by step I_{b1} .

As shown in Tables 3 and 7, step I_a on Pt or Rh film is as slow as step I_b at low temperature in contrast with the cases of $Cu^{1)}$ and $Ni^{2)}$ films, with which step I_a is concluded to be far faster than the rate-determining step I_b . Slow step I_a has also been observed by BOND *et al.*¹⁴⁾ with alumina-supported Pt and Rh catalysts. Step I_a thus looks like to rate-control the steady hydrogenation. However, in the case of a reaction of single route¹⁵⁾ involving an irreversible step, forward rate of the step is always equal to the overall reaction rate but the step is not necessarily rate-controlling; *e.g.*, step III of scheme (1) is perfectly irreversible but not rate-controlling

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at low temperatures as shown in the previous works.^{1,2)} Adsorption of ethylene on Pt catalyst has been found to be irreversible by SMITH and MERRILL¹⁶⁾ and WEINBERG *et al.*¹⁷⁾ with LEED and helium beam scattering. Furthermore, ethylene hydrogenation on Pt and Rh catalysts obeys the rate law⁴⁾ $V_s \propto P_H^1 P_E^0$ (P_H or P_E denotes partial pressure of hydrogen or ethylene, respectively), suggesting step I_b being rate-determining similarly to the cases of Cu¹⁾ and Ni²⁾ catalysts. Accordingly, surface of Pt and Rh catalysts may be nearly saturated by strongly adsorbed ethylene, and step I_a is practically rate-controlled by step I_b which rate-determines ethylene hydrogenation. Ethylene adsorbs more strongly on Pt film than on Rh film and a reversibility of step I_a , *i. e.*, $v_-(I_a)/v_+(I_a)$, on both metals increases with rise of reaction temperature as seen from Tables 3 and 7.

Catalytic deactivation of Pt and Rh films observed at low temperature is probably not caused by any impurities in reactant, since Ni film is not deactivated at 0°C with the same reactant. Deactivation of Rh film for ethylene hydrogenation and accompanying P_2 - D_2 equilibration is more remarkable at low temperature or low partial pressure of hydrogen, while hydrogen mixing between C_2P_4 and C_2D_4 is not so remarkably retarded as shown in Figs. 4 a), b) and c). With Pt film hydrogen mixing in ethylene is unmeasurably slow. These facts are understood as that step I_b is strongly retarded by adsorption of ethylene with fall of temperature or hydrogen pressure, while hydrogen mixing in ethylene can take place *via* step II of scheme (1) so far as adsorbed hydrogen atoms are present on catalyst surface.

In the previous work with Ni film²⁾ it has been shown that the rate-determining step of ethylene hydrogenation shifts from step I_b to III at the so-called optimum temperature, where $v_-(I_b)$ equals to $v_+(III)$.³⁾ Figure 1 suggests that $v_-(I_b)$ increases with rise of reaction temperature to be equal to $v_+(III)$ at *ca.* 190°C, which is close to the optimum temperature 160°C observed by FARKAS and FARKAS¹⁸⁾ or 240°C by KAZANSKII and STRUNIN.¹⁹⁾

Results of the present and previous works^{1,2)} are summarized in Table 9, which shows that $v_+(I_b)/V_s$ is smaller than $v_+(I_a)/V_s$ and $v_+(II)/V_s$ for every metals and the latter two become smaller with increase of the catalytic activity of metal. The value of $v_+(I_a)/V_s$ is supplemented as given in Table 10 by the results evaluated from the observations of BOND *et al.*^{14,20)} with alumina-supported metal catalysts, Pt, Ir, Ru, Os, Pd and Rh. Relatively large value of $v_+(I_a)/V_s$ for Rh as compared with Table 9 is due to rapid evolution of deuterioethylene at the initial stage of reaction probably caused by dissociative adsorption of ethylene. Table 11 shows relative catalytic

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TABLE 9. Relative activities of evaporated Rh, Pt, Ni²⁾ and Cu¹⁾ films for ethylene deuteration and relative rates of respective steps.

Metal	Activity*)	Temp. (°C)	$v_+(I_a)/V_s$	$v_+(I_b)/V_s$	$v_+(II)/V_s$
Rh	1.0	0	1.4	1.2	7.0
		80	1.8**)	—	—
Pt	1.8×10^{-2} **)	85	1.6	1.2	15.8
Ni	2.4×10^{-2}	79	6.4	1.1	26.6
Cu	3.0×10^{-6} **)	78	74.7	2.0	38.1

*) Rate of ethylene deuteration at 0°C per unit geometrical surface area of evaporated metal film ($V_s(\text{Rh}) \equiv 1.0$).

***) Value estimated by extrapolation.

TABLE 10. Relative rate of step I_a evaluated from the results of BOND *et al.*^{14,20)}

Metal	Temp. (°C)	P_E P_H		$v_+(I_a)/V_s$
		(mmHg)		
Pt	54	99	98	1.3
Ir	86	100	100	1.2
Ru	80	75	76	3.5
Os	36	50	50	1.6
Pd	67	100	100	4.9
Rh	76	100	100	6.4

P_E, P_H : initial partial pressure of ethylene and deuterium.

TABLE 11. Relative activities of metals for ethylene hydrogenation measured by SCHUIT and VAN REIJEN²¹⁾, BEECK²²⁾ and KEMBALL²³⁾; log activity (Rh) $\equiv 0$.

Catalyst form	Temp. (°C)	log activity						
		Rh	Ru	Pd	Pt	Ni	Ir	Cu
on SiO ₂ ²¹⁾	0	0	-0.3	-0.9	-1.5	-1.5	-2.0	-4.1
film ²²⁾	0	0	—	-0.8	-1.65	-2.6	—	—
film ²³⁾	-100	0	—	—	—	-1.0	—	—

activities of metals for ethylene hydrogenation ever observed.²¹⁻²³⁾ These results are summarized in Fig. 5 with the log-log plots of catalytic activity against $v_-(I_a)/V_s (= v_+(I_a)/V_s - 1)$. With regard to the metals on the right of Rh in this figure, the order of catalytic activity for ethylene hydrogenation

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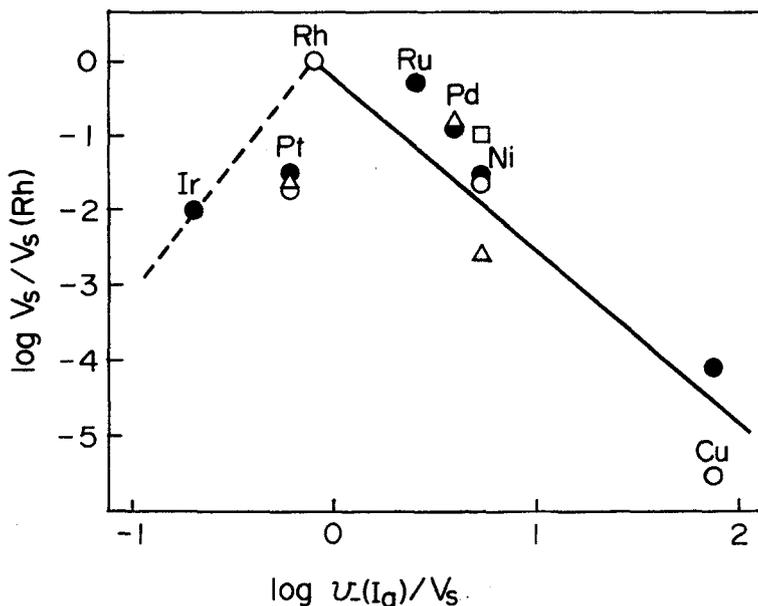


Fig. 5. Relation between catalytic activity ($V_s/V_s(\text{Rh})$) of metal for ethylene hydrogenation and $v_-(I_a)/V_s$ ($67 \sim 86^\circ\text{C}$).

Pt, Rh, Ni, Cu, Present and previous^{1,2}) results; Ir, Ru, Pd, BOND *et al.*,^{14,20}) catalytic activities of which are referred to SCHUIT and VAN REIJEN²¹) (●), BEECK²²) (△) or KEMBALL²³) (□).

is parallel to that for $\text{P}_2\text{-D}_2$ equilibration²¹) or *para*-hydrogen conversion,²⁴) as expected from the present and previous^{1,2,4}) conclusion that hydrogen chemisorption (step I_b of scheme (1)) rate-determines ethylene hydrogenation. The $\text{P}_2\text{-D}_2$ equilibration is faster than ethylene hydrogenation by a factor of *ca.* 2 with Cu¹), *ca.* 10 with Ni²⁵) and *ca.* 300 with Pt, suggesting that hydrogen chemisorption is retarded more strongly by adsorbed ethylene with decrease of $v_-(I_a)/V_s$. Accordingly, the decrease of hydrogenation activity of the metals on the left of Rh in Fig. 5 may be caused by strong adsorption of ethylene as discussed before. A volcano-type correlation given in Fig. 5 is consequently understood as that hydrogenation activity of metal is determined by two factors; activity of metal for hydrogen chemisorption and irreversibility or strength of ethylene adsorption on metal.

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