HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS

Part 9—The Reaction over Evaporated Tungsten Films

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Abstract

Hydrogenation of ethylene catalyzed by evaporated tungsten film was observed at temperatures between $-45°C$ and $100°C$ with regard to its rate, adsorbed amounts of hydrogen and ethylene in course of the reaction and deuterium distribution in hydrogen and ethylene at the early stage of deuteration of light ethylene.

Observations of the adsorption and the deuterium distribution indicate, unlike the case of evaporated nickel film, that the hydrogenation is attended with dehydrogenated adsoption of ethylene of a considerable extent even at $-45°C$ irrespective as to whether the tungsten film is freshly evaporated, once used for the reaction and evacuated at room temperature or reduced by deuterium after the latter treatment and evacuated similarly at $300°C$. Deuterium preliminarily adsorbed was actively exchanged with protium in gaseous hydrogen or ethylene.

The deuterium was found randomly distributed in hydrogen, but not in ethylene both at $-45°C$ and $100°C$, which indicates that the step of hydrogen chemisorption is kept in equilibrium, but the set of steps leading to hydrogen exchange of ethylene is not.

The optimum temperature, *ca.* $20°C$, was observed over reduced tungsten film with regard to the hydrogenation of *ca.* 0.4 mmHg light ethylene by equimolar protium and its activation heat was found 8.2 kcal/mole at temperatures below the optimum.

The number of sites of the critical system of the rate-determining step of ethane formation was found to be 10^{15} per unit surface area of reduced tungsten film, indicating that the whole surface is active in catalyzing the ethane formation, in spite of a pronounced dehydrogenated adsorption of ethylene, which possibly results in an appreciable coverage of the surface with acetylenic complex or carbonic deposit rendering more or less sites incompetent.

Introduction

Tungsten is known to catalyze hydrogenations and hydrogen exchanges of several hydrocarbons, but its behaviour as a catalyst differs considerably

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from those of transition metals; for instance, the rate and the activation heat of ethylene hydrogenation on tungsten at 0°C was, as observed by BEECK,[1] extraordinarily small as compared with those on transition metals. Considerable amount of deuteroethylenes including d_4-ethylene, *i. e.* C_2D_4, was formed in course of catalyzed deuteration of light ethylene at −100°C on Rh, Ni or Fe, but not on W, where there was formed just a small amount of d_1-ethylene, *i. e.* $C_2^1H_3D$, but none of d_n-ethylene of $n > 1$.[2] Tungsten was found much less active than transition metals in catalyzing hydrogenolysis of amines at 200°C.[3]

Tungsten is, on the other hand, most active in catalyzing the hydrogen exchange between deuterium and light methane,[4] ethane[5] or catalytic hydrogenolyses of paraffins.[6] Another peculiarity of tungsten as catalyst is the lower limit of the number, *i. e.* $10^6 cm^{-2}$, of sites of critical system of the rate-determining step as derived from the statistical mechanical analysis of kinetic data of the exchange reaction between methane and deuterium,[7] which is exceptionally small as compared with its average, *ca.* $10^{15} cm^{-2}$, derived from 66 available cases of experimental data.[7]

With special reference to these peculiar catalytic behaviours of tungsten the catalyzed reaction between ethylene and hydrogen in its presence was invsetigated in the present work in comparison with the previous results[2] of nickel catalyst, on which basis the mechanism of the reaction was discussed.

Experimental

The apparatus, materials and experimental procedure were similar to those in the previous works[8] excepting the preparation of evaporated tungsten film.

A tungsten wire of 0.2 mmϕ and *ca.* 30 cm in length was mounted in the reaction vessel of 130 cc capacity, heated at 500°C by an electric furnace in *ca.* 40 mmHg deuterium gas for *ca.* 14 hr and evacuated for 15 hr as far as 5×10^{-7} mmHg, while the wire was heated with *ca.* 4.5 A a. c.; the wire was now evaporated for 40 min by passing 6.0 A a. c. through the wire, immersing the reaction vessel in a salt bath at 300°C. The wire was subjected to the above treatment and evaporated for 10 min in case where the wire was evaporated to coat the film previously evaporated. A film thus freshly evaporated either directly on the glass wall or on a previously evaporated film is denoted by F and that once used for reaction and evacuated to $5-7 \times 10^{-7}$ mmHg at room temperature by S in what follows. R similarly signifies film S used for the reaction, evacuated to $5-7 \times 10^{-7}$ mmHg at room temperature, reduced at 300°C in *ca.* 15 mmHg deuterium gas for an hour or longer and finally evacuated to 5×10^{-7} mmHg for 30 min at 300°C.

A run of reaction on film F, S or R was conducted, similarly as in the previous work,[8] immersing the reaction vessel in a bath kept at a desired temperature, by introducing into it a known amount of one to one mixture of light ethylene and protium, deuterium or their mixture. The bath of water or melting monochlorobenzene was used for the reaction at 0°C and above or at −45°C respectively. Course of the total pressure was now recorded by means of a Pirani gauge and a pen-recorder, usually for the first short period, and after a recorded time of the reaction a part of the reacted gas was diffused into a sampling vessel for mass spectrometric analysis; the negative initial inclination of the total pressure derived from the record was taken for a measure of the initial rate of deuteration or hydrogenation. The course of deuterium distribution in hydrogen and ethylene was observed by a series of runs at *ca.* 0.7 mmHg total pressure and at −45°C, each conducted for a different time over one and the same tungsten film reduced prior to the run by deuterium at 300°C and evacuated to 5×10^{-7} mmHg.

The mass spectrometric analysis was conducted quite similarly to the previous work;[8] the relative amounts of $^1H_2$, ^1HD and D_2 in reacted gas were approximated by the relative heights of peaks of mass numbers, 2, 3 and 4 respectively at the electron accelerating voltage, V_e, of 70 volt and those of d_n-ethylenes ($n = 0, 1, \cdots, 4$) by the relative heights of peaks of mass numbers, 28, 29, $\cdots$, 32, obtained at $V_e = 13.5$ volt, where the mass spectrum of ethylene consists of parent peaks alone. The deuterium distribution in ethane was not observed on account of its insufficient yield for the mass spectrometric analysis.

Results

Table 1 shows the deuterium distribution in hydrogen and ethylene in course of deuteration of light ethylene at −45°C on films, F, S and R respectively; the "Reacted %" is the percentage of the observed total pressure decrease at the moment of sampling on the initial partial pressure of ethylene calculated to be a half of the initial total presure, P_0, V_0 the initial rate of the observed total pressure decrease and the parenthesized figures the relative amounts for random distribution of deuterium atoms in hydrogen or ethylene respectively calculated on the base of observed deuterium atomic fraction, y_H or y_E, of hydrogen or ethylene.

Points of the result are summarized below.

(1) Table 1 shows that V_0 over R lies intermediate between those over F and S irrespective of the period of reduction, and slightly decreases by repetitions of run of the reaction each followed by reduction and evacuation

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TABLE 1. Deuterium distribution in gaseous hydrogen and ethylene formed by reactions of equimolar mixture of D_2 and light ethylene at $-45°C$ over freshly evaporated (F), once used (S) and reduced (R) tungsten films.

P_0*) (mmHg)	State of film	Reacted (%)	V_0**) (mmHg/min)	d_n-Hydrogen (%)			d_n-Ethylenes≡E_n (%)					D-atomic fraction	
				$^1H_2$	^1HD	D_2	E_0	E_1	E_2	E_3	E_4	y_H	y_E
0.07	F	63	0.782	1.3	4.4	94.3	39.0	19.5	22.0	7.3	12.2	0.965	0.335
				(0	6.7	94.3)	(19.5	39.5	29.7	10.1	1.2)		
	S	41	0.441	0.2	3.9	96.0	61.6	15.4	12.1	3.3	7.7	0.978	0.201
				(0	4.3	95.7)	(41.0	41.0	15.3	2.6	0.2)		
	R, 1.0 hr***)	47	0.561	1.5	3.9	94.5	48.6	17.1	17.1	5.7	11.4	0.960	0.285
0.07	F	54.5	0.752	1.8	6.7	91.5	35.5	16.0	25.8	9.7	12.9	0.948	0.371
	S	38.3	0.481	1.2	4.5	94.3	55.0	15.0	17.5	5.0	7.5	0.965	0.263
	R, 1.3 hr	50.0	0.516	1.2	5.1	93.6	50.0	18.5	18.5	3.7	9.3	0.962	0.259
	R, 2.5 hr	41.7	0.511	1.5	4.9	93.6	72.5	10.9	7.2	2.2	7.2	0.960	0.152
	R, 15.0 hr	32.7	0.500	1.9	3.5	95.6	84.2	7.9	5.3	0	2.6	0.963	0.072
0.57	F	8.6	0.274	0.7	3.1	96.2	86.7	9.2	2.1	0.8	1.2	0.978	0.052
				(0	4.5	95.5)	(80.0	18.5	1.6	0.6	0)		
	R, 1.0 hr	10.5	0.256	0.8	3.9	95.4	84.0	10.4	2.9	0.9	1.8	0.974	0.065
	R, 18.5 hr	11.6	0.155	0.6	3.3	96.1	87.5	8.9	1.8	0.6	1.2	0.978	0.048

*) P_0 is the pressure derived from the amount of gas initially introduced and the volume of the reaction vessel assuming the ideal gas law ; 0.100 mmHg of P_0 corresponds to 6.33×10^{17} molecules at $-45°C$.

**) Initial deuteration rate derived from decrease of total pressure.

***) Time of reduction with *ca.* 15 mmHg deuterium at 300°C.

to 5×10^{-7} mmHg.

(2) The deuterium distribution in hydrogen and ethylene, *i. e.* the relative amounts of $^1H_2$, ^1HD and D_2 in hydrogen and those of d_n-ethylenes, are respectively nearly the same in every case of films F, S and R.

(3) Table 1 shows that the deuterium distribution in ethylene of runs of $P_0=0.07$ mmHg at $-45°C$ over film F is wide of random one and d_n-ethylenes are alternately abundant at $n=0$, 2 and 4. The similar tendency of d_n-ethylenes is potentially perceptible in cases of films S and R at $P_0=0.07$ mmHg. At higher P_0 as shown in Fig. 1 a, the relative amounts of d_2- and d_4-ethylenes on film R, are constantly larger than that of d_3-ethylene from the initial stage of the reaction and d_2-ethylene predominates over d_1-ethylene after the elaspe of *ca.* 40 sec of reaction time, revealing the similar deuterium
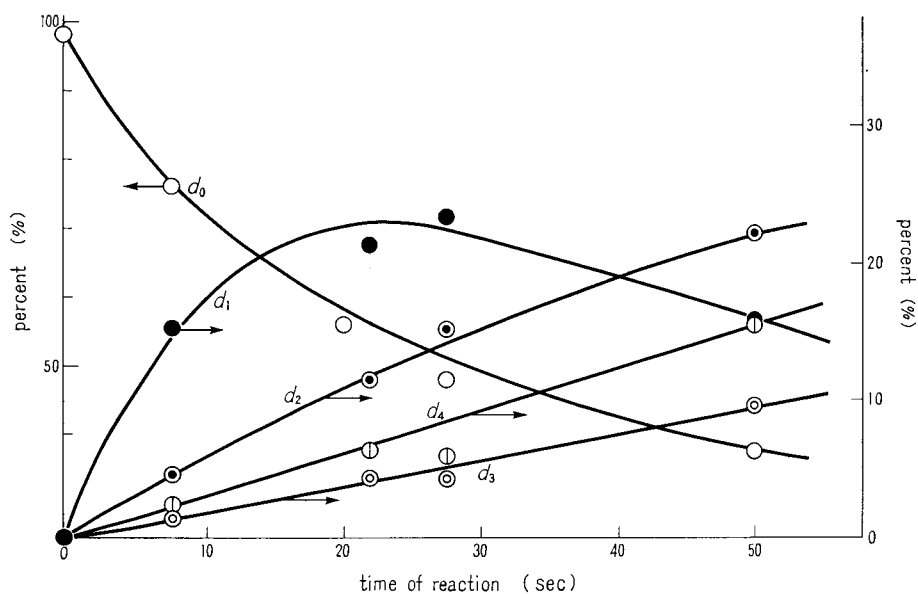
Fig. 1 a. Courses of relative amounts of respective d_n-ethylenes formed by reaction between equimolar light ethylene and deuterium catalyzed by tungsten film R at $-45°C$ and $P_0=0.7$ mmHg.
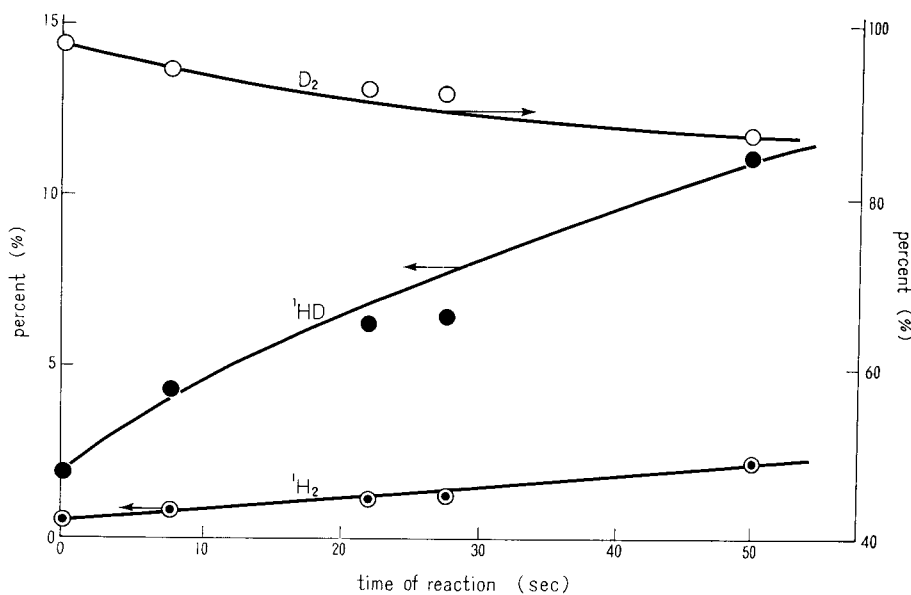

Fig. 1 b. Courses of relative amounts of $^1H_2$, ^1HD and D_2 formed by reaction between equimolar light ethylene and deuterium catalyzed by tungsten film R at $-45°C$ and $P_0=0.7$ mmHg.

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distribution to that in case of film F mentioned above. Table 2 shows that at 100°C and $P_0 = 0.8$ mmHg on film R d_3-ethylene never exceeds d_2- and d_4-ethylenes similarly to the case of the result in Fig. 1 a.

(4) The deuterium distribution in hydrogen is practically random as seen from Tables 1, 2 and 3 ;[*] Table 3 indicates that the equilibration of the mixture of D_2 and $^1H_2$ is immediately attained on its contact with film R at -45°C in the presence of light ethylene.

(5) In runs of $P_0 = 0.07$ mmHg the observed initial pressure was much less than P_0 on any of films F, S and R, which indicates that a considerable adsorption sets in immediately after the introduction of the reactant mixture over the film. Table 4 shows the amount of hydrogen or ethylene adsorbed on film R at -45°C, which was derived as the excess of the amount of hydrogen (or ethylene) initially introduced into the reaction vessel over the sum of those of hydrogen (or ethylene) and ethane existing in reacted gas;

TABLE 2. Deuterium distribution in hydrogen and ethylene derived from equimolar mixture of light ethylene and D_2 kept over film R at 100°C.

P_0 (mmHg)	State of film	Reacted (%)	V_0 (mmHg/min)	Hydrogen (%)			d_n-Ethylene≡E_n (%)					D-atomic fraction	
				$^1H_2$	^1HD	D_2	E_0	E_1	E_2	E_3	E_4	y_H	y_E
0.8	R, 56.0 hr	12.1	2.27	1.7	14.6	83.7	56.5	24.0	13.0	3.2	3.3	0.910	0.181
				(0.8	16.4	82.8)	(45.0	39.8	13.3	1.9	0)		
	R, 1.0 hr	10.5	2.00	1.6	13.2	85.2	65.3	22.3	9.0	1.8	2.6	0.928	0.142
	R, 2.0 hr	5.6	1.71	1.4	10.4	88.2	69.1	19.3	6.9	1.9	2.8	0.934	0.125

TABLE 3. Deuterium distribution in gaseous hydrogen and ethylene formed by reations of equimolar mixture of light ethylene and $D_2 + {}^1H_2$ at -45°C over film R.

P_0 (mmHg)	State of film	Reacted (%)	V_0 (mmHg/min)	Hydrogen (%)			d_n-Ethylene≡E_n (%)					D-atomic fraction	
				$^1H_2$	^1HD	D_2	E_0	E_1	E_2	E_3	E_4	y_H	y_E
0.7	R, 1.0 hr	6.70	0.133	9.5	34.2	56.3	88.9	7.0	2.3	1.1	0.7	0.734	0.045
				(7.1	38.9	54.0)	(83.2	15.7	1.1	0	0)		
	R, 1.0 hr	7.70	0.136	9.1	35.0	55.9	88.6	7.2	2.4	1.1	0.7	0.734	0.046
Initial mixture				16.8	1.7	81.5	97.8	2.2	0	0	0	0.823	0.005

*) The percentage of $^1H_2$ may be too large on account of the mass spectrometric superposition of D⁻.

TABLE 4. Adsroption of protium and light ethylene in course
of their reaction at $-45°C$ over film R.

Number of molecules initially introduced	State of film	Reacted (%)	$^1H_2$ adsorbed (molecules)	$C_2{}^1H_4$ adsorbed (molecules)
1.31×10^{18}	R, 1.0 hr	37.2	1.61×10^{16}	1.45×10^{16}
1.71×10^{18}	,,	79.3	-1.27×10^{17}	0.32×10^{17}
1.71×10^{18}	,,	33.3	-0.44×10^{17}	2.85×10^{17}
1.71×10^{18}	,,	30.4	-1.57×10^{17}	3.10×10^{17}
1.71×10^{18}	,,	20.0	-1.71×10^{17}	3.80×10^{17}
1.71×10^{18}	,,	28.1	-1.58×10^{17}	3.55×10^{17}
1.71×10^{18}	,,	8.2	-1.96×10^{17}	4.56×10^{17}
1.71×10^{18}	,,	11.9	-1.96×10^{17}	3.49×10^{17}
1.71×10^{18}	,,	13.3	-1.96×10^{17}	3.10×10^{17}
2.44×10^{18}	,,	70.0	-1.30×10^{17}	1.04×10^{17}

this excess gives the adsorbed amount exactly, provided that the hydrogenation of ethylene to ethane is only reaction that takes place and that ethane is not at all adsorbed in the presence of ethylene as verified in a previous work.[9] The amount of adsorbed hydrogen thus derived presents, with its sign reversed, the lower limit to the amount of hydrogen gas evolved by the dehydrogenated adsorption of ethylene. The latter lower limit decreases with rise of temperature as seen from Table 5.

(6) In case where tungsten film was preliminarily reduced by deuterium and evacuated to 2–3×10^{-6} mmHg, considerable amount of deuterated hydrogen and hydrocarbons, inclusive of D_2 and C_2D_6, were found at the early stage of reaction between light ethylene and protium conducted over the same film at $P_0 = 0.07$ mmHg and $-45°C$; hydrogen gas was completely equilibrated also in this case with regard to the deuterium distribution. Deuterosubstitution product was not at all found in the case where a film reduced by D_2 was preliminarily evacuated to 5×10^{-7} mmHg for 30 min.

(7) Table 5 presents the hydrogenation rate, the composition of reacted gas and "the adsorbed amounts of hydrogen and ethylene"*) at the early stage of the reaction between light ethylene and protium over film R at $P_0 = 0.8$ mmHg at different temperatures. We see from the Table that the excess of hydrogen in reacted gas over ethylene is the greater, the lower the reaction temperature.

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*) *Cf.* point (5).

TABLE 5. Temperature dependences of composition of reacted gas, amounts of adsorbed hydrogen and ethylene and hydrogenation rate of the equimolar mixture of protium and light ethylene over film R.

Time (sec)	Temp. (°C)	Number of molecules ($\times 10^{18}$)			Composition of reacted gas (%)			Adsorbed amount ($\times 10^{17}$ molecules)		Hydrogenation rate (10^{16} molecules/sec)	
		Introduced	Descrease*)	$C_2{}^1H_6$ formed**)	$^1H_2$	$C_2{}^1H_4$	$C_2{}^1H_6$	$^1H_2$	$C_2{}^1H_4$	Decreases of gas	$C_2{}^1H_6$ formation
25.0	−45	4.91	0.71	0.57	50.8	35.6	13.6	−2.55	3.24	2.84	2.29
7.0	−25	4.91	0.76	0.64	44.5	40.0	15.5	−0.35	1.52	10.85	9.19
10.0	−25	4.91	0.76	0.72	48.2	34.4	17.4	−2.69	3.02	7.60	7.30
2.4	0	4.72	0.79	0.70	43.9	38.4	17.7	−0.69	1.54	33.8	30.0
2.2	20	4.42	1.11	0.92	40.5	31.8	27.7	−0.45	2.42	51.2	42.5
3.4	50	4.37	1.23	1.14	31.3	32.3	36.4	0.63	0.32	36.9	34.4
4.4	74	4.32	1.41	1.16	30.4	29.7	39.9	0.29	0.50	32.6	26.8
4.4	97	4.12	1.35	0.91	34.6	31.6	32.8	1.33	2.18	31.2	21.0

*) In gas phase derived from the total pressure decrease.
**) In gas phase derived from the total pressure and the composition of reacted gas sampled.

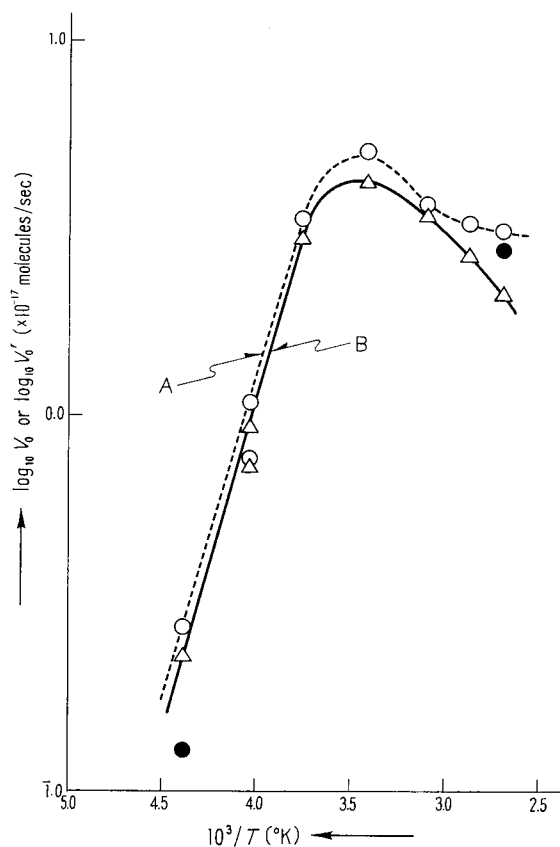**Fig. 2.** Arrhenius plot of the rate of hydrogenation of light ethylene by equi-
molar protium (○ and △) or deuterium (●) at $P_0=0.8$ mmHg over
tungsten film R; curve A or B is that of the rate of the total pressure
decrease, V_0, (○) or of the rate of ethane formation, V_0', (△) respec-
tively in the hydrogenation by protium (*Cf.* Table 5).

(8) Fig. 2 shows the Arrhenius plots of the hydrogenation rates ; curve
A or B is the Arrhenius plot of V_0 or the rate, V_0', of ethane formation.
They nearly coincide with each other at lower temperatures giving practically
the same values of optimum temperature, *ca.* 20°C, and of activation heat,
8.2 kcal/mole, over the temperature below the optimum.

(9) The ratio of hydrogenation rate, V_0, of light ethylene to its deutera-
tion rate is derived from the result of Fig. 2 as *ca.* 2.1 at -45°C and 1.1 at
97°C over film R as observed with one to one mixture of ethylene and protium
or deuterium at $P_0=0.8$ mmHg.

Discussions

It has been known that hydrogen was irreversibly adsorbed up to full coverage of the surface[10] and hydrogen thus adsorbed was capable of being exchanged to any extent with gaseous hydrogen.[11] Point (6) of the foregoing section states, on the other hand, that the hydrogen irreversibly adsorbed is very active in hydrogenation of ethylene as well as in hydrogen exchange with gaseous hydrogen. The random distribution of deuterium in gaseous hydrogen stated in point (4) verifies, in conjunction with point (6), that the chemisorption of hydrogen

$$H_2 \longrightarrow 2H(a) \qquad\qquad\qquad (1)$$

is in equilibrium in course of ethylene hydrogenation over the temperature range from $-45°C$ to $100°C$, which amply embraces the optimum temperature, *ca.* $20°C$.

The negative value of "the amount of adsorbed hydrogen"[*] in Tables 4 and 5 indicates a pronounced evolution of hydrogen by dehydrogenated adsorption of ethylene over film R; this contrasts with the case of nickel film,[9] where "the amount of adsorbed hydrogen"[**] was positive throughout in conformity with the observed absence of dilution of deuterium gas by protium in course of deuteration of light ethylene on either of nickel films S and R.

Large amount of deuteroethylene of every extent of deuterosubstitution was formed at $-45°C$ in the present experiments as shown in Table 1 and Fig. 1 a, in contrast with the result of KEMBALL[2] that deuteroethylene was scarcely formed in deuteration of light ethylene over tungsten film at $-100°C$. As regards point (3) the exchange through step

$$C_2H_4 \longrightarrow C_2H_2(a) + 2H(a) \qquad\qquad (2)$$

and its reverse ought to be taken into account. $^1H(a)$ formed by the forward act of step (2) are immediately replaced by D(a) through step (1) in equilibrium in the initial stage of the reaction between D_2 and $C_2{}^1H_4$, so that d_2- and d_4-ethylenes are preferentially formed by the backward act of step (2), provided that *cis* hydrogen atoms of ethylene molecule are removed or restored by the forward or the backward act of step (2) respectively. The formation of d_1- and d_3-ethylenes may be assigned to the appearance of $^1H(a)$ in the later stage of reaction and/or to the concurrent "stepwise hydrogen exchange" of ethylene,

$$C_2H_4 \longrightarrow C_2H_3(a) + H(a) \qquad\qquad (3)$$

and/or

*) *Cf.* point (5).
**) *Cf.* point (5).

$$C_2H_4(a) + H(a) \longrightarrow C_2H_5(a) . \tag{4}$$

None of steps (2), (3) and (4) ought to be in equilibrium on account of the wide deviation of the deuterium distribution in ethylene from random one and of the considerable difference between y_H and y_E as seen in Tables 1, 2 and 3, since, if otherwise, any of these steps in equilibrium would work with step (1) in equilibrium to render the deuteroethylene a random distribution and the value of y_E coincident with y_H.

The lower limit to the number of sites, N^*, of the critical system of the rate-determining step of ethane formation over film R is now derived according to the procedure developed in the previous work[7] on the base of activation heat, 8.2 kcal/mole, of ethane formation at temperatures below the optimum, the rate, 3.26×10^{16} molecules·sec^{-1}, of ethane formation at $-45°C$, and the proportionality of the rate of ethane formation to the partial pressure of hydrogen alone as derived from the observation of BEECK[1] over evaporated tungsten film at 0°C. The lower limit was thus found to be 5.0×10^{19} to the total number of sites on the whole surface of film R. The lower limit to the number of sites per unit area is hence calculated at 10^{15}–10^{16} on the base of the roughness factor, 10–10^2,[*] and *ca.* 150 cm^2 apparent area of the film. The number of sites is in consequence 10^{15} cm^{-2}, with reference to its upper limit, 10^{15} cm^{-2}, defined by the crystallographic number of surface metal atoms. The whole surface of the film is hence active in catalyzing the ethane formation.

AZUMA and ISHIZUKA[12] have found by field emmision microscopic study that ethylene adsorbed on tungsten was decomposed by evacuation at temperatures above 300°C to leave carbonic deposit on the surface, which was enhanced by contacting the adsorbed ethylene preliminarily with hydrogen. Taking this fact into consideration it may be conceived that ethane formation by the reaction of ethylene with gaseous hydrogen as well as with H(a)'s formed by steps (2) and (3) proceeds on tungsten surface covered by "acetylenic complex", which leaves by evacuation some carbonic deposit on the surface which poisons further hydrogenation of ethylene. We thus understand point (1) on the differences among V_0-values over the films F, S and R.

It is concluded from point (8) of the approximate coincidence of the rate

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*) According to the observation of BEECK (*Advances in Catalysis* **2**, p. 151 (1950)) the roughness factor of a surface of tungsten film evaporated onto glass wall kept at liquid air temperature was 10^3 by order of magnitude and five times as large as that of nickel film evaporated under the same condition. We found the roughness factor 3 for nickel film evaporated on glass wall kept at 200°C, hence the roughness factor of the present tungsten film evaporated at 300°C was thus estimated on account of it being rather stable against sinter due ot its higher melting point.

of ethane formation with that of total pressure decrease, that ethane is formed by such reactions as

$$C_2H_4 + H_2 \longrightarrow C_2H_6 \qquad\qquad (5)$$

and

$$2\,C_2H_4 \longrightarrow C_2H_2(a) + C_2H_6\,, \qquad\qquad (6)$$

but reactions consuming ethylene otherwise, *e. g.* polymerization or carbonization of ethylene, if any, do not matter at temperatures below the optimum.

We could not so far observe the steady hydrogenation of ethylene over tungsten film to the exclusion of dehydrogenated adsorption of ethylene ; what is concluded for the present is that the rate-determining step of the hydrogenation of ethylene on W catalyst may, unlike the nickel catalyst, serve for that of formation of deuteroethylene as well throughout reaction temperatures below and above the optimum, on the ground that the deuterium distribution was random in hydrogen but not in ethylene.

Acknowledgments

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