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HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS

Part 7—Qualitative Verification of the Rate-Diagram Theory of HORIUTI by Deuteration of Light Ethylene on Evaporated Nickel Film

By

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Abstract

The rate-diagram theory of HORIUTI[1] on the hydrogenation of ethylene catalyzed by nickel states the rate-determining step switches over from Ib to III of the Scheme

$$\begin{array}{l} C_2H_4 \xrightarrow{Ia} C_2H_4(a) \\ H_2 \xrightarrow{Ib} \begin{cases} H(a) \\ H(a) \end{cases} \end{array} \Bigg\} \xrightarrow{II} C_2H_5(a) \Bigg\} \xrightarrow{III} C_2H_6$$

at the optimum temperature with rise of temperature, where (a) denotes the adsorbed state. This theory has been qualitatively verified by observation of the initial rate of deuteration of light ethylene catalyzed by evaporated nickel film and deuterium distribution in reacted hydrogen and ethylene. The nickel film was the used one, *i.e.* that beforehand used once for deuteration and evacuated at the reaction temperature, on which the concurrent dissociative adsorption of ethylene was practically suppressed at low temperatures as concluded in the foregoing work[2].

Temperature dependence of the kinetical isotopic effect, *i.e.* a ratio of hydrogenation rate of light ethylene by protium to that by deuterium, has been observed on the same nickel film at *ca.* 0.1 mmHg total pressure, resulting in qualitative agreement with the conclusion of the rate-diagram theory.

Deuteration on carbided nickel film has resulted, in distinction from in the case of used film, in dilution of deuterium gas by equilibrated protium atoms at tempreatures below and above the optimum, revealing a large pressure dependence of its activation heat at temperatures below the opimum and a temperature independent kinetical isotopic effect in the same temperature range, which is larger than that on used film throughout the range. These results and the previous ones[2][3], *i.e.* extremely small hydrogenation rate and such adsorbed amount of hydrogen as compared with in the case of used film suggest some other mechanism of hydrogenation of ethylene on carbided film than the rate-diagram theory on used film.

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Introduction

In the previous papers[2)3)4)] it has been found that the catalyzed hydrogenation of ethylene on nickel catalyst was made appreciably reproducible by the uses of nickel film evaporated onto a glass wall kept at 200°C and pure hydrogen and ethylene mass spectrometrically free from water, oxygen or nitrogen and, furthermore, that[2)] the dissociative adsorption of ethylene concurrent with the hydrogenation on freshly evaporated nickel film was practically suppressed in the case of used film at temperatures below the optimum. The used film is an evaporated nickel film used beforhand once for the hydrogenation and evacuated at the reaction temperature. These results makes the used film being preferable to the fresh one for the analysis of mechanism of the catalyzed hydrogenation of ethylene on nickel catalyst as concluded in the previous work[2)].

The mechanism of the reaction has now been deduced from the previous results[2)] of the deuteration of light ethylene catalyzed by the used nickel film, resulting in the qualitative verification of the rate-diagram theory of HORIUTI[1)]. The observed temperature change of the kinetical isotopic effect of hydrogenation on the used nickel film has also resulted in the qualitative agreement with the conclusion of the rate-diagram theory.

The reproducible condition of the catalyzed hydrogenation of ethylene on evaporated nickel film has also been investigated by JENKINS and RIDEAL[5)], who have found that this conditon was attained by the use of a carbided nickel film formed by preliminary heating of an evaporated nickel film in ethylene at 190°C and discussed on its basis the mechanism of the catalyzed hydrogenation of ethylene on nickel catalyst. It has been found, on the other hand, by the present author that the carbided nickel film was distinctly different from the used one in its catalytic behaviour in hydrogenation of ethylene, *i.e.* the hydrogenation rate[3)6)], the adsorbed amount of hydrogen in course of the hydrogenation[2)], the optimum temperature[3)6)], the activation heat below the optimum temperature[3)] and the kinetical isotopic effect and its temperature change[3)].

Further investigation of the carbided nickel film has now been made, under the same experimental condition as in the foregoing observation[2)] with the used film, on the kinetical isotopic effect mentioned above and the deuterium distribution in hydrogen and ethylene formed by deuteration of light ethylene. It has been found that the carbided nickel film was also distinctly different from the used one with regards the large kinetical isotopic effect and the total pressure dependence of the activation heat at temperatures below the optimum and the equilibrated distribution of protium atoms in deuterium gas in course

of deuteration of light ethylene.

Experimental

The hydrogenation rate of light ethylene on used nickel film was followed, succesively to the foregoing experiment of deuteration[2], at temperatures between −45°C and 150°C, and thus the temperature change of the kinetical isotopic effect was determined. The film was then carbided by using it repeatedly for hydrogenation at 200°C each followed by evacuation at the same temperature, and then hydrogenation and deuteration of light ethylene were conducted on one and the same carbided nickel film at temperatures between −23°C and 160°C. The experimental condition was quite the same as in the previous experiment[2] except the case of carbided film which was evacuated after each run at 200°C to 1×10^{-6} mmHg and then the next run was conducted immersing the reaction vessel into an oil bath kept at a specified temperature. Hydrogenation were similarly conducted on one and the same carbided film with equimolar mixture of light ethylene and hydrogen at 0.16, 0.67 and 1.20 mmHg total pressure at temperatures between 0°C and 120°C to examine the total pressure dependence of the activation heat of hydrogenation of ethylene on carbided film.

Results

Table 1 reproduces the results[2] previously obtained by deuteration of light ethylene at *ca.* 0.1 mmHg total pressure on used film, denoting protium or deuterium by P or D respectively. Parenthesized values under the Column "Deuterium distribution" of the Table are relative amounts of respective deutero-substituted hydrogen and ethylene calculated assuming the random distribution of deuterim atoms for the values of deuterium atomic fractions y_H and y_E of hydrogen and ethylene respectively as given in the last column of the Table.

Table 2 shows the results of the present experiment on carbided nickel film.

Fig. 1 shows the previous[2] and the present results of temperature changes of the initial rates of hydrogenation and deuteration on used and carbided nickel films; sign P_2(II) or P_2(C) annexed to each curve denotes hydrogenation on (II) used or (C) carbided film respectively and D_2(II) deuteration on used film. Curve D_2(C) is the result of the present experiment of deuteration on carbided film. Activation heats of hydrogenation and deuteration at temperatures below the optimum on carbided film are equally 2.5 Kcal/mole, which is remarkably smaller than 11 Kcal/mole previously observed on the same film at 20 mmHg initial

TABLE 1. Deuterium distribution in hydrogen and ethylene formed by deuteration of light ethylene on used nickel film.

React. temp. °C	Rate of deutepation $-C_2H_4$ %/min.	Deuteration %	Deuterium distribution								Deuterium atomic fraction	
			Hydrogen, %			Ethylene, %						
			P_2	PD	D_2	C_2P_4	C_2P_3D	$C_2P_2D_2$	C_2PD_3	C_2D_4	y_H	y_E
− 45	3.5	2	0	1.6	98.4	93	7	0	0	0	0.992	0.017
			(0	1.6	98.4)	(93	7	0	0	0)		
− 23	18.2	10	0	1.6	98.4	90	10	0	0	0	0.992	0.025
			(0	1.6	98.4)	(90	10	0	0	0)		
0	56.9	20	0	6	94	64	30	6	0	0	0.970	0.105
			(0	6	94)	(64	29	5	2	0)		
28	98.0	43	2	10	88	66	28	5	1	0	0.930	0.103
			(0	13	87)	(65	30	5	0	0)		
32	107.1	41	10	19	71	40	36	20	4	0	0.805	0.220
			(4	31	65)	(37	42	18	3	0)		
75	97.0	38	30	29	41	29	38	24	7	2	0.555	0.263
			(20	49	31)	(30	42	20	5	3)		
110	50.2	21	14	39	47	21	29	37	10	2	0.665	0.340
			(11	45	44)	(19	30	38	10	2)		

TABLE 2. Deuterium distribution in hydrogen and ethylene formed by deuteration of light ethylene on carbided film.

React. temp. °C	Rate of deuteration $-C_2H_4$ %/min.	Deuteration %	Deuterium distribution								Deuterium atomic fraction	
			Hydrogen, %			Ethylene, %						
			P_2	PD	D_2	C_2P_4	C_2P_3D	$C_2P_2D_2$	C_2PD_3	C_2D_4	y_H	y_E
− 23	0.86	1.2	2	4	94	88	12	1	0	0	0.970	0.032
2	1.26	1.0	3	6	91	80	18	2	0	0	0.956	0.055
70	3.16	6.4	53	40	7	16	32	32	15	4	0.272	0.368
110	3.75	3.1	53	40	7	19	32	32	14	3	0.272	0.340
160	2.12	3.1	50	42	8	21	32	31	13	3	0.293	0.323

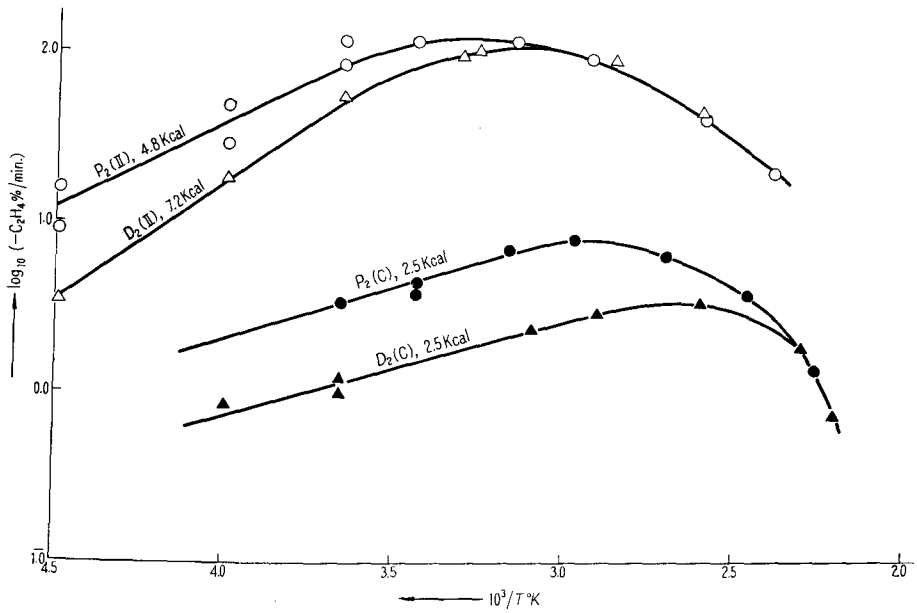

Fig. 1. ARRHENIUS plots of hydrogenation rates P_2(II) or P_2(C) by protium and D_2(II) or D_2(C) by deuterium on (II) used or (C) carbided nickel film respectively.

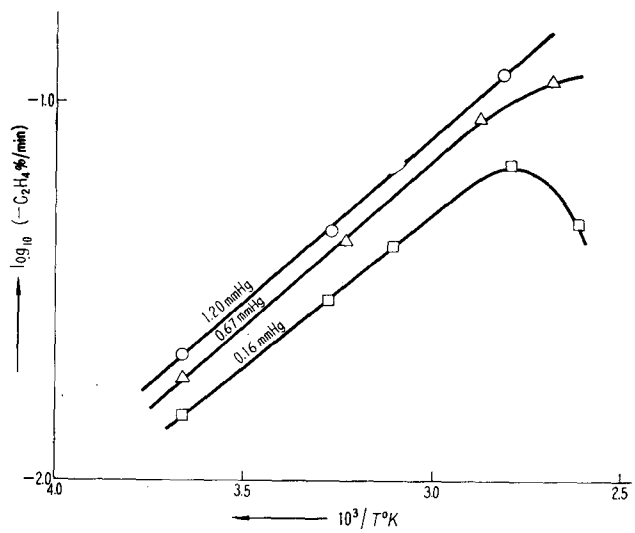

Fig. 2. ARRHENIUS plots of hydrogenation rates on carbided nickel film at 0.16, 0.67 and 1.20 mmHg total pressures respectively.

total pressure[6]. Fig. 2 shows the ARRHENIUS plots of the hydrogenation rate on carbided film at 0.16, 0.67 and 1.20 mmHg total pressures, from which the activation heat is determined at 3.9 Kcal/mole for the first case and 4.3 Kcal/mole for the second and the third ones respectively. In contrast with this, activation heat in case of used film is practically independent on total pressure as seen from the present result in Fig. 1 at *ca.* 0.1 mmHg and previous ones 6.0 and 8.4 Kcal/mole[3] for P_2(II) and D_2(II) respectively both at *ca.* 20 mmHg initial total pressure.

Fig. 3 shows the temperature dependence of the kinetical isotopic effect of the hydrogenation calculated on the basis of the results of Fig. 1.

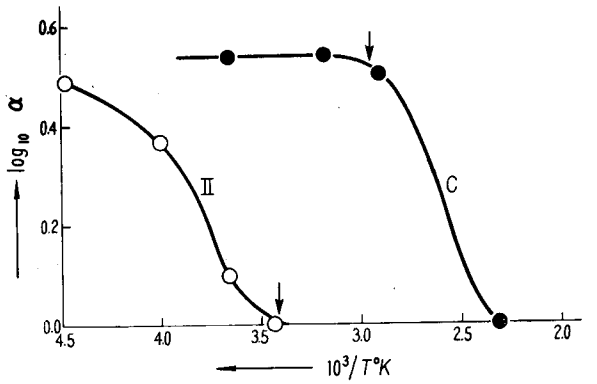

Fig. 3. Temperature dependences of the kinetical isotopic effect α of hydrogenation of ethylene on (II) used and (C) carbided films respectively; arrow shows the optimum point of hydrogenation by P_2.

Discussion

It has been observed in the previous experiments[2)7)] that appreciable amounts of hydrogen and ethylene were adsorbed on the used nickel film. The observed hydrogen exchange between deuterium and light ethylene in course of deuteration may then be attributed to the steps that

$$C_2H_4 \longrightarrow C_2H_4(a), \qquad \text{(Ia)}$$

$$H_2 \longrightarrow 2H(a) \qquad \text{(Ib)}$$

and

$$C_2H_4(a) + H(a) \longrightarrow C_2H_5(a) \qquad \text{(II)}$$

with neglection of the concurrent dissociative adsorption of ethylene according to the previous conclusion[2], where H stands for protium P or deuterium D respectively and (a) denotes the adsorbed state. Steps Ia and II are now be

in equilibrium irrespective of the reaction temperature because deuterium atoms transferred into ethylene are always in random distribution as seen from Table 1.

The initial value 0.992 of y_H of deuterium gas remained, on the one hand, unchanged at $-45°C$ or $-23°C$ in spite of progress of formation of ethane and deuterosubstituted ethylenes as seen from Table 1. This fact indicates that the backward rate of hydrogen chemisorption Ib is negligibly small compared with its forward rate and rates of other steps exclusive of that of ethane formation.

$$C_2H_5(a)+H(a) \longrightarrow C_2H_6\,, \qquad \text{(III)}$$

and consequently Ib is rate-determining in these cases.

Table 1 shows, on the other hand, that deuterium gas was markedly admixed by protium at temperatures near and above the optimum. If this dilution of deuterium gas by protium were caused by steps Ia, Ib and II mentioned above, these steps give rise to a rapid exchange of hydrogen adatoms with abundant protium from light ethylene and in consequence to H(a)'s consisting mainly of protium; protium should thus be transferred into hydrogen gas preferentially as P_2 but not PD in the case when Ib is constanly rate-determining. The intervention of concurrent dissociative adsorption of light ethylene, if any, should lower the deuterium content of H(a)'s and multiplies the balanced forward and backward rates of step II, and thus ensures the above conclusion. The fact that the observed deuterium distribution in hydrogen gas approached to that of equilibrium with rise of temperature, indicates that the step Ib is no more rate-determining but in equilibrium at high temperature similarly as steps Ia and II, and consequently the step III of ethane formation becomes the slowest one with rise of temperature. These equilibrated steps other than III should give rise to a random distribution of deuterium adatoms in hydrogen and ethylene and hence to the equality of values of y_H and y_E. This conclusion is in comformity with the result of Table 1 that values of the deuterium atomic fractions of hydrogen and ethylene approach with each other with rise of temperature. The backward rate of III is neglected on the basis of the theoretical conclusion[1] as well as the experimental results that ethane was not adsorbed under coexistence of gaseous ethylene[7] and that the amount of initially admixed deuteroethane was unchanged in course of hydrogenation of light ethylene on nickel wire at 50°, 100° and 150°C[8].

The mechanism concluded above is very the rate-diagam theory of HORIUTI[1], which states that the rate-determining step switches over at the optimum temperature from Ib to III keeping the steps Ia and II constantly in equilibrium.

The rate-diagram theory is, furthermore, supported by the results of the

present and previous experiments as follows. The optimum temperature of hydrogenation of light ethylene by equimolar protium gas shifted from *ca.* 100°C[3] of the previous results to *ca.* 30°C of the present one with decrease of the initial total pressure from *ca.* 20 mmHg to *ca.* 0.1 mmHg. Such pressure change of the optimum temperature agrees quantitatively with the previous conclusion[6] of the rate-diagram theory. The temperature change of the kinetical isotopic effect of hydrogenation on used fiilm shown by Curve II of Fig. 3 is also in qualitative agreeement with the conclusion[3] of the rate-diagram theory, which states that the kinetical isotopic effect of hydrogenation of light ethylene should be present or absent at temperatures below or above the optimum respectively according to the step Ib of hydrogen chemisorption being rate-determining or not.

The result of Table 2 obtained by carbided film differs, on the other hand, from that of used film with regards the deuterium distribution in hydrogen gas, which is random even at low temperatures. It has been found, furthermore, by previous and present experiments as regards the carbided nickel film in comparison with the used film that (1) the amount of ethylene adsorption is much the same but hydrogen is not perceptively adsorbed in course of hydrogenation[4], that (2) the optimum temperature is *ca.* 30°C higher and the rate of catalyzed hydrogenation is more than ten times smaller[3)6)], that (3) the kinetical isotopic effect is similarly unity or greater than unity respectively above or below the optimum but it remains constant for carbided film below the optimum different from the case of used film as shown in Fig. 3 and that (4) the activation heat is more sensitive to the total pressure of 1 : 1 mixture of hydrogen and ethylene as observed to be 2.5, 3.9, 4.3 or 11 Kcal/mole at the total pressure of 0.10, 0.67, 1.20 or 20 mmHg respectively. It may be inferred on the bases of the above results that the mechanism of hydrogenation of ethylene on carbided film probably differs from that on used one.

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