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## HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS

### Part 10—The Reaction on Evaporated Iridium Film

By

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#### Abstract

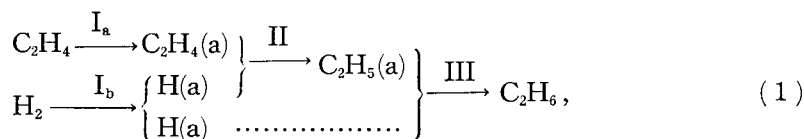
The initial rate of ethylene hydrogenation on evaporated iridium film in equimolar mixture with hydrogen was observed at *ca.* 0.5 mmHg of total pressure and at temperatures between  $-45^{\circ}\text{C}$  and  $100^{\circ}\text{C}$ .

An optimum temperature was found at *ca.*  $50^{\circ}\text{C}$  and the activation heat at the lower temperature region was *ca.* 3 kcal/mole. The amounts of ethylene and hydrogen adsorbed in the middle stage of the hydrogenation were found to be nearly constant, independent of reaction temperature.

From data on the deuterium distribution in the deuterated product of light ethylene a conclusion was drawn that the mechanism proposed by HORIUTI *et al.* for the case of nickel catalyst at low temperature region is valid in this case, but this was accompanied by a reversible dissociative adsorption of ethylene, and hence of self-hydrogenation of ethylene, which became significant at temperatures above the optimum.

#### Introduction

The presence of so-called "optimum temperature" is well known in the hydrogenation of ethylene catalyzed by nickel and this has been interpreted as a temperature at which the rate-determining step of the hydrogenation switches over with rise of the reaction temperature from I<sub>b</sub> to III in the following reaction scheme,<sup>1)2)</sup>



where (a) denotes an adsorbed state.

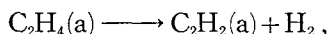
On the basis of the above mechanism, various experimental results such as the dependence of the optimum temperature on nickel catalyst upon partial

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pressure of ethylene,<sup>3)</sup> kinetic behaviour of associated reactions,<sup>2)</sup> *e. g.*, parahydrogen conversion, deuterium exchanges between hydrogen and ethylene, relative rates of formation of respective deuterio-substitutes *etc.*, have been well interpreted.

The optimum temperature was similarly observed in ethylene hydrogenation on platinum,<sup>4)</sup> palladium,<sup>4)</sup> copper,<sup>5)</sup> iron<sup>6)</sup> and tungsten<sup>7)</sup> catalyst. In the case of tungsten catalyst, however, such a shift of the rate-determining step at the optimum temperature was disproved<sup>7)</sup> on the basis of the fact that a mixture of light and heavy hydrogen, when it was used for hydrogenation, was isotopically completely equilibrated at the very early stage of the hydrogenation even at temperatures far lower than the optimum.

The optimum temperature, *ca.* 300°K, observed in the case of tungsten catalyst has recently been discussed by RYE<sup>8)</sup> with reference to his observation of hydrogen evolution from heated tungsten catalyst which was preliminarily once brought into contact with ethylene at 95°K. He thus observed<sup>9)</sup> two maxima, at *ca.* 300°K and 450°K respectively, in the rate of hydrogen evolution, and concluded, with reference to the difference between the amount of ethylene preliminarily adsorbed and that of the hydrogen evolved, that the hydrogen evolution with its maximum at 300°K was caused by the partial decomposition of adsorbed ethylene, *i. e.*



and the other, which became noticeable above 300°K, by successive decomposition of  $\text{C}_2\text{H}_2(\text{a})$  to  $\text{H}_2$  and carbon which deposits on the catalyst surface. RYE<sup>9)</sup> has hence attributed the optimum temperature on tungsten catalyst to the decay of the catalytic activity caused by poisoning effect of the carbon deposition which would be significantly accelerated at temperatures above the optimum. Further, he extended this theory to the case of iridium catalyst and predicted that no optimum temperature should be observed in this case at temperatures below *ca.* 400°K, because of absence<sup>10)</sup> of any appreciable decomposition of adsorbed ethylene to carbon in this temperature region.

In the present work hydrogenation and deuteration of light ethylene on iridium film were investigated with particular interest on the RYE's prediction on the optimum temperature.

### Experimental and Results

The apparatus and the experimental procedures are similar to those used in the previous experiments.<sup>7)</sup> Iridium was evaporated onto the inner surface of the reaction vessel of 130 cc volume, immersed in a salt bath at 300°C,

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from an iridium wire of 0.1 mm diameter and 10 cm length, which was preliminarily reduced with 40 mmHg hydrogen for 15 hr at 500°C and then evacuated down to  $7 \times 10^{-7}$  mmHg at the same temperature.

In each run a known amount of 1:1 mixture of light ethylene and hydrogen was introduced into the reaction vessel and the gas phase pressure was followed by a Pirani-gauge. The initial rate of hydrogenation was evaluated from the initial inclination of this time course of the pressure. At a recorded time, a portion of the reacting gas was quickly sampled for mass-spectrometric analysis. The conversion or the extent of hydrogenation was evaluated as the ratio of the amount of ethane found in the gas phase over that of ethylene initially introduced into the reaction vessel. The amounts of ethylene and hydrogen adsorbed at the time of sampling were evaluated on the basis of mass balances with respect to ethylene and hydrogen between the reactant mixture originally introduced into the reaction vessel and the reacting gas in the vessel at the time of sampling, assuming that ethylene is exclusively converted into ethane and the latter is not adsorbed in the presence of the former similarly to the case of nickel catalyst.<sup>11)</sup> The results are given in Table 1, where F, S or R in the column of "No. of run"

TABLE 1. Initial rate of ethylene hydrogenation and amounts of ethylene and hydrogen adsorbed in the middle stage of the reaction on evaporated iridium film. (*ca.* 0.5 mmHg initial total pressure of 1:1 mixture of H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>)

No. of run	Temp. °C	Amount of reactant introduced, 10 <sup>17</sup> molecules	Initial rate of hydrogenation, 10 <sup>16</sup> molecules/sec	Pressure at the time of sampling, mmHg	Conversion, %	Amounts of adsorption, 10 <sup>-17</sup> molecules	
						C <sub>2</sub> H <sub>4</sub>	H <sub>2</sub>
F	-25	27.10	2.22	0.376	45.5	1.50	2.00
S	-25	19.80	1.28	0.314	42.4	-0.07	0.32
R 1	-25	20.15	2.21	0.280	41.6	1.01	1.88
R 2	-45	20.80	1.23	0.301	27.4	1.78	1.58
R 3	0	19.35	3.87	0.280	39.1	2.77	1.82
R 4	20	19.50	4.61	0.273	53.6	1.48	1.36
R 5	50	20.80	5.85	0.328	51.1	1.05	1.05
R 6	75	19.73	4.96	0.328	40.6	2.36	0.86
R 7	98	18.90	4.67	0.328	36.7	2.04	0.68
R 8	50	20.30	6.03	0.321	42.6	2.29	0.63
R 9	20	20.15	4.41	0.314	33.6	1.83	1.53
R 10	0	19.00	3.64	0.294	22.0	1.48	1.99

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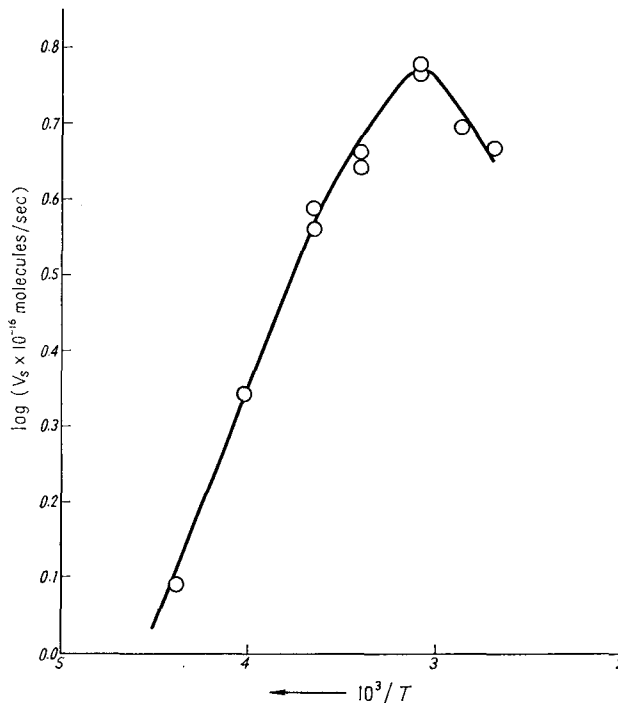


Fig. 1. ARRHENIUS plot of the initial rate of hydrogenation on reduced iridium film (cf. data of R series in Table 1).

indicates, respectively, a run conducted on iridium film freshly evaporated, once used for the hydrogenation and evacuated at the reaction temperature or reduced with *ca.* 20 mmHg hydrogen and evacuated both at 300°C successively to the preceding run.

In order to elucidate the mechanism of ethylene hydrogenation on iridium catalyst the distribution of deuterium in the products of hydrogenation of light ethylene with an 1.1 : 0.9 mixture of hydrogen and deuterium was investigated at temperatures far lower and higher than the optimum, *i. e.*,  $-25^{\circ}\text{C}$  and  $100^{\circ}\text{C}$ , respectively. The results are given in Table 2, where  $y_D(\text{H})$ ,  $y_D(\text{E})$  and  $y_D(\text{A})$  are the deuterium atomic fraction of hydrogen in hydrogen (H), ethylene (E) and ethane (A) in the reacted gas, respectively; the figures in the parenthesis are those calculated for the case of random distribution of deuterium in H, E or A, respectively.

### Discussion

Results of the first three runs in Table 1 show, on the one hand, that

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TABLE 2. The deuterium distribution in the product of hydrogenation of light ethylene with an 1.1 : 0.9 mixture of  $^1\text{H}_2$  and  $\text{D}_2$  on iridium film. (ca. 0.5 mmHg initial total pressure)

No. of run	Temp. °C	Conversion, %	Relative amounts of deuterioisotopes, %							
			Hydrogen (H)			Ethylene (E)				
			$^1\text{H}_2$	$^1\text{HD}$	$\text{D}_2$	$\text{C}_2^1\text{H}_4$	$\text{C}_2^1\text{H}_3\text{D}$	$\text{C}_2^1\text{H}_2\text{D}_2$	$\text{C}_2^1\text{H}_3\text{D}$	$\text{C}_2\text{D}_4$
R 11	-25	27	55.4 (31.6)	1.4 49.2	43.2 19.2)	96.0 (96.1)	3.9 3.9	trace 0	0 0	0 0)
R 12	100	33	57.1 (40.2)	14.4 46.4	29.4 13.4)	84.0 (71.0)	6.4 25.3	4.3 3.4	3.2 0.2	2.1 0)
Composition of reactant			54.2	1.2	44.5	100	0	0	0	0

Ethane (A)							Deuterium atomic fraction		
$\text{C}_2^1\text{H}_6$	$\text{C}_2^1\text{H}_5\text{D}$	$\text{C}_2^1\text{H}_4\text{D}_2$	$\text{C}_2^1\text{H}_3\text{D}_3$	$\text{C}_2^1\text{H}_2\text{D}_4$	$\text{C}_2^1\text{H}_2\text{D}_5$	$\text{C}_2\text{D}_6$	$y_{\text{D}}(\text{H})$	$y_{\text{D}}(\text{E})$	$y_{\text{D}}(\text{A})$
28.0 (24.7)	35.6 38.9	21.2 25.5	11.1 8.9	2.1 1.8	1.2 0.2	0 0)	0.438	0.01	0.208
48.6 (41.9)	32.8 39.2	8.6 15.3	7.6 3.2	2.1 0.4	0 0	0 0)	0.366	0.08	0.135
0	0	0	0	0	0	0	0.451	0	0

the initial rate of hydrogenation decreased to about one half and the amounts of adsorbed ethylene and hydrogen significantly decreased from F to S. The initial rate of hydrogenation as well as the amounts of adsorption on film F, on the other hand, was practically reproduced by film R. These facts show that some products, presumably formed by decomposition and/or polymerization of ethylene, occupy the iridium surface and hence retard the adsorption of both ethylene and hydrogen. However, these products are easily removed from the surface by hydrogenation as compared with the cases of other metallic catalysts, *e.g.*, Ni,<sup>12)</sup> Fe<sup>6)</sup> and W,<sup>7)</sup> where the initial rate of hydrogenation on film F was never reproduced by film R.

It is seen from Fig. 1 that the optimum temperature exists at ca. 50°C, against RYE's prediction<sup>8)</sup> mentioned in the Introduction. Further, according to RYE's theory, hydrogen should be evolved into gas phase by decomposition of adsorbed ethylene at temperatures above the optimum and hence the amounts of adsorbed hydrogen, as estimated according to mass

balances mentioned above, should noticeably decrease at such temperatures. However, the amounts of adsorbed ethylene and hydrogen were changed not so much with rise of the reaction temperature from  $-45^{\circ}\text{C}$  to  $98^{\circ}\text{C}$ . RYE's theory is thus denied in this case.

The activation heat of hydrogenation on film R at the lower temperature region was evaluated at *ca.* 2.9 kcal/mole from Fig. 1.

It is seen from Table 2 that at  $-25^{\circ}\text{C}$  the deuterium distribution in hydrogen, on the one hand, is nearly the same as that in the initial hydrogen, *i.e.*, evolution of hydrogen from species on the catalyst surface is not significant in course of the hydrogenation of ethylene. The deuterium distribution in ethylene and ethane, on the other hand, is nearly random. On the basis of these results it is concluded that hydrogen is atomically added to ethylene and the hydrogenation at  $-25^{\circ}\text{C}$  proceeds through scheme (1) with step  $I_b$  being rate-determining and steps  $I_a$ , II and III in quasi-equilibrium. The mechanism thus concluded is quite similar to the previously proposed one for nickel catalyst.<sup>1)2)</sup>

The deuterium distribution in hydrogen obtained at  $100^{\circ}\text{C}$  shows that step  $I_b$  of scheme (1) is still not in its equilibrium at such a temperature far higher than the optimum, in sharp contrast with the cases of evaporated Ni,<sup>11)12)</sup> Fe<sup>6)</sup> and W<sup>7)</sup> films. The formation of highly deuterated ethylene and ethane, with the deuterium distribution far differing from the random one, suggests simultaneous occurrence of deuterium exchange through a reaction other than scheme (1), probably dissociative adsorption of ethylene. Species on iridium surface possibly contributing to such an exchange may be easily removed by hydrogenation, as seen from the results of the first three runs given in Table 1.

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