The Catalytic Hydrogenation of Ethylene at a Nickel Surface. Part II.* The Reaction Mechanism.

By G. I. Jenkins and Sir Eric Rideal.

The evidence for the mechanism of the hydrogenation of ethylene on nickel advanced in Part I is supported by experiments on nickel films which have been pre-treated to form respectively partly complex-covered and partly " carbided " surfaces. The formal reaction kinetics over a wide range of temperatures and partial pressures of the reacting gases are likewise found to be in conformity with the mechanism proposed.

In Part I * it was shown by measurement of gas adsorption on nickel films that when the metal is exposed to ethylene gas the surface becomes progressively covered with acetylenic residues until some 80% of the surface is so covered. In the presence of hydrogen a further 10% of the complex-covered surface can adsorb hydrogen, whilst the residual 10% consists presumably of isolated sites which may be covered with hydrogen atoms by migratory processes within the metal. Further, the hydrogen thus adsorbed is readily removed by gaseous ethylene to form ethane. No evidence of the presence of chemisorbed ethylene as such was found.

We might infer that during active catalysis this hydrogen-accessible 10% of the surface alone is the operative area, since the slow rehydrogenation of the surface complexes has been found to furnish but a minor contribution, the main reaction consisting of the chemisorption of hydrogen and its removal by gaseous ethylene to form ethane.

Any completely satisfactory scheme for the molecular mechanism must permit us to interpret the following experimental facts on which there appears to be general agreement : (1) Over the temperature range investigated the reaction velocity is proportional to the pressure of hydrogen gas. (2) According to the detailed studies of zur Strassen (*Z. physikal. Chem.*, 1934, *A*, **169**, 81) and Toyama (*Rev. Phys. Chem. Japan*, 1937, **11**, 153; 1938, **12**, 115) the rate is proportional to the ethylene pressure at high temperatures and independent thereof at room temperatures. (3) A maximum is observed in the rate–temperature curve, and this maximum appears to move to higher temperatures with increasing ethylene pressures (Rideal, *J.*, 1922, **121**, 309; Melville, *J.*, 1934, 803; zur Strassen, *loc. cit.*). (4) Admission of ethylene at 20° results in a self-hydrogenating reaction and an acetylenic complex is left on the surface. At higher temperatures this complex can be converted into carbide as first shown by Sabatier. (5) Ethane does not influence the reaction (Rideal, Toyama, Beeck). (6) There is in addition an exchange reaction with deuterium and a migration of the double bond in such olefins as butene.

A number of investigators have commenced their studies with clean nickel wires or films. We would expect that the reactivity of a nickel surface would be initially high, falling to a constant value as the ethylene complex builds up to its final stationary coverage. In many systems diffusion processes may limit the rate of reaction and it was considered important to investigate these two points in some detail as well as confirm the kinetics which the majority of investigators have found.

* Part I, preceding paper.

EXPERIMENTAL

Preliminary work with the small reaction vessel (30 c.c. volume with a 50-mg. metal film, cf. Part I, *loc. cit.*) showed that even at 20° the effects of gas diffusion on the reaction velocity were considerable (*i.e.*, no appreciable increase in rate on increasing the temperature). Since this involved diffusion of reactant gases from the connecting tubes, a magnetically driven glass centrifugal pump was introduced into the circuit. As seen in Fig. 1, the rate of hydrogenation in a mixture of hydrogen and ethylene (5·6 cm. pressure of each gas) was found to be dependent on the speed of the pump. This offers an explanation for the results obtained by Palmer and Palmer (*Proc. Roy. Soc.*, 1921, *A*, **99**, 402). The reaction system was accordingly redesigned so that no dead space was present and a smaller weight of nickel evaporated.

Commencing with a fresh catalyst a reaction mixture of the two gases in equal proportions was added (4·0 cm. pressure), and the rate of reaction determined for 10 min. at 20°. The

FIG. 1.

FIG. 2.
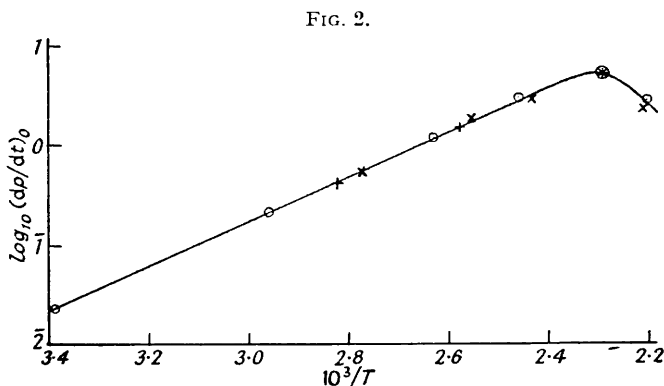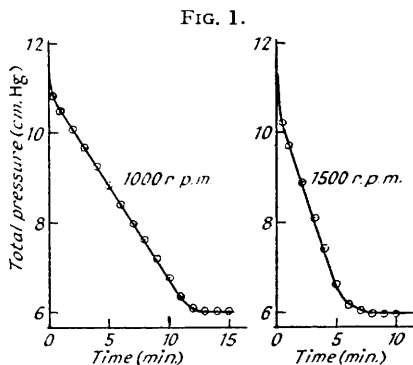
gases were then removed, and a fresh gas mixture admitted. The initial rates of reaction were found to be as in Table 1a. In every experiment the velocity of reaction reached a constant and reproducible value after one or two runs, the first being more rapid.

TABLE 1.

		(a) With a fresh catalyst				(b) With a catalyst pre-treated with ethylene		
Run No.	1	2	3	4	5	1	2	3
Rate (mm. Hg/min.)	3·50	1·90	1·30	1·30	1·30	1·60	1·30	1·40

In a further series of experiments the nickel catalyst was first exposed to ethylene gas at 4·0 cm. pressure for 30 min. at 20° before examining it for catalytic activity. This treatment, as expected, almost eliminated the initial fast reaction (Table 1b). The catalytic activity of a complex-covered surface was compared with that of a " carbided " surface formed by heating a complex-covered catalyst. The hydrogen adsorption on these two catalysts at 5×10^{-3} mm. pressure and 20° was 6·5 and 2·5 units respectively, whilst the rates of hydrogenation of ethylene at 4·0 cm. pressure and 20° were 0·60 mm./min. and 0·20 mm./min. respectively.

The close connection between the hydrogen adsorption and rate of reaction receives further

support from the results of experiments in which minute amounts of oxygen were admitted to the gas mixture. Rideal (*J.*, 1922, **121**, 309) showed that traces of oxygen in the gas mixture cause an induction period in the reaction during which the oxygen is preferentially hydrogenated to water. At 20°, in the presence of traces of oxygen, the induction period was found to be 240 sec. on a complex-covered catalyst and 600 sec. on a carbided catalyst, whilst the ratio of the active quantities of hydrogen adsorbed was 6·5 to 2·5.

Nickel films which had been exposed to ethylene for 30 min. at 190° were found to be very reproducible in behaviour.

The surface having been carbided, runs were made with the gases in equal proportions at 5 cm. Hg partial pressure over the range 20—180°. In Fig. 2 are given the details of runs on three different catalysts of different areas (after correction for the area) which have been

FIG. 3.
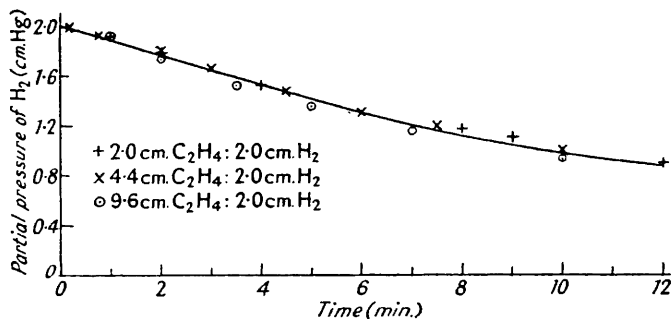
FIG. 4.
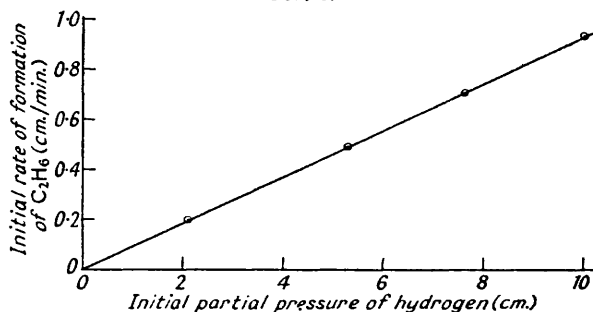
treated in this way. In accord with other workers, the energy of activation at low temperatures is found to be 10·2 kcal./mole and there is an inversion temperature at 160—165°.

On varying the partial pressures of the reacting gases the initial rates were found to conform to the relationship

$$(T_{165°}) \quad \text{Rate} = AP_{H_2}P_{C_2H_4}/(1 + BP_{C_2H_4})$$

The extent of agreement between experimental and calculated rates is given in Table 2. Below the inversion temperature the rate of reaction was independent of the ethylene pressure when that was varied from 2·0 to 9·6 cm. pressure but was directly proportional to the pressure of hydrogen as shown in Figs. 3 and 4.

Thus $(T_{114°C})$ Rate $= KP_{H_2}$.

TABLE 2.

Initial pressures (cm. Hg)		Initial rates at 165° (mm./min.)		Initial pressures (cm. Hg)		Initial rates at 168° (mm./min.)	
C_2H_4	H_2	obs.	calc.	C_2H_4	H_2	obs.	calc.
2·1	1·9	0·7	0·9	2·1	1·9	0·7	0·9
5·0	2·0	1·3	1·5	3·0	5·3	3·0	3·3
9·8	2·0	1·9	1·9	2·8	9·8	6·0	6·0
3·0	5·3	3·0	3·3	5·0	2·0	1·3	1·5
5·2	5·3	4·5	4·2	5·2	5·3	4·5	4·2
10·6	4·8	4·4	4·6	4·8	10·4	9·0	8·1

DISCUSSION

The comparative kinetics on complex-covered and "carbided" surfaces evidently supports the experimental evidence given in Part I (*loc. cit.*) in favour of the view that gaseous ethylene reacts with hydrogen chemisorbed on paired sites which occupy only some 10% of the surface of the nickel catalyst. If θ denotes the fraction of paired sites on which hydrogen is chemisorbed, we can write for the rate of chemisorption of hydrogen $k_1 P_{H_2}(1 - \theta)$. The chemisorbed hydrogen can either evaporate at a rate $k_2\theta$ or react with gaseous ethylene at a rate $k_3 P_{C_2H_4}\theta$. Under steady-state conditions

$$k_1 P_{H_2}(1 - \theta) = k_2\theta + k_3 P_{C_2H_4}\theta$$

Hence the rate of hydrogenation will be

$$k_3 P_{C_2H_4}\theta = \frac{k_1 k_3 P_{H_2} P_{C_2H_4}}{k_2 + k_3 P_{C_2H_4} + k_1 P_{H_2}} \qquad \qquad (1)$$

Evidently if $k_1 P_{H_2}$ is small compared to $k_2 + k_3 P_{C_2H_4}$ and $k_3 P_{C_2H_4} \simeq k_2$, then

$$\text{Rate} = \frac{k_1 k_3 P_{H_2} P_{C_2H_4}}{k_2 + k_3 P_{C_2H_4}} = \frac{A P_{H_2} P_{C_2H_4}}{1 + B P_{C_2H_4}} \qquad \qquad (2)$$

If further, at low temperatures, $k_3 P_{C_2H_4} \gg k_2$

$$\text{Rate} = k_1 P_{H_2} \qquad \qquad (3)$$

Thus the change in kinetic behaviour from dependence on the hydrogen pressure alone at low temperatures to one involving both hydrogen and ethylene at higher temperatures as shown by Toyama, zur Strassen, and in these experiments, can be interpreted on the basis that on elevation of the temperature the rate of evaporation of hydrogen $k_2\theta$ increases more rapidly than the reaction with ethylene $k_3 P_{C_2H_4}\theta$, *i.e.*, the former (k_2) must have a higher energy of activation than the latter (k_3). At the temperature at which the velocity of hydrogenation undergoes an apparent inversion it is clear that $k_2 \approx k_3 P_{C_2H_4}\theta$ or $k_2/k_3 P_{C_2H_4} \approx 1$. Since k_2 increases more rapidly with the temperature than k_3, evidently the inversion temperature will be higher the higher the partial pressure of ethylene. Zur Strassen, working at 0·03—0·2 mm. Hg, recorded an inversion temperature of 90°. Others have found higher inversion temperatures with increase in pressure. The present experiments give 160—165° at 40 mm. Hg.

At still higher temperatures $k_2 \gg k_3 P_{C_2H_4}$, and the rate of reaction will become

$$(k_1 k_3/k_2) P_{H_2} P_{C_2H_4}$$

a relationship found by both zur Strassen and Toyama over their highest ranges of temperature.

It is also possible to envisage the exchange reaction between deuterium and the hydrogen in ethylene, which has long been accepted as related to the hydrogenation of ethylene, taking place in a similar manner. The following mechanism is proposed for exchange.

There are two methods of determining the rate of the exchange reaction of $C_2H_4 + D_2$, the first actually determining the deuterium content of the ethylene (Turkevich, Schissler, and Irsa, *J. Phys. Colloid Chem.*, 1951, **55**, 1078) (*i.e.*, reaction 2), and the second determining the hydrogen gas in the gas phase (Farkas, Farkas, and Rideal, *Proc. Roy. Soc.*,

1934, *A*, **146**, 630 ; Twigg, Thesis, and Rideal and Twigg, *Proc. Roy. Soc.*, 1939, *A*, **171**, 55) (*i.e.*, reaction 3).

The relative rates of hydrogenation and exchange (method 2) are given by $k_3 P_{C_2H_4}$ and k_2 respectively, k_2 being much smaller at low temperatures but of comparable magnitude at 165°. In experimental agreement, the temperature coefficient of the exchange reaction is much greater than that of hydrogenation, both rates being comparable at 170°.

It is also possible to correlate the results of Turkevich (*loc. cit.*) and Rideal and Twigg (*locc. cit.*). The hydrogen leaving the catalyst in the initial stages of Twigg's experiments on $C_2H_4 + D_2$ at 100—160° was almost pure hydrogen. The exchange reaction rate (reaction 2) must therefore be considerably faster than the rate of desorption of hydrogen from the surface, so that all the deuterium adsorbed has exchanged with hydrogen (contributed by the ethylene) before desorption. Thus at 170° the following picture is obtained. Deuterium is adsorbed on the catalyst on the few " active " sites. There is a rapid exchange reaction (reaction 2) which is much faster than the desorption of hydrogen or the hydrogenation reaction. Initially the deuterium on the surface is completely replaced by hydrogen. If reaction 2 is also faster than the hydrogenation at lower temperatures, then the *rapid* replacement of the deuterium on the surface by hydrogen contained in the ethylene will mean that the main product initially in hydrogenation is C_2H_6 and not $C_2H_4D_2$; *i.e.*,

$$C_2H_4(g) + D_2(g) \xrightarrow{\text{Ni}} C_2H_4(g) + 2NiD$$

$$2NiD + 2C_2H_4(g) \xrightarrow[\text{Fast}]{} 2NiH + 2C_2H_3D(g)$$

$$2NiH + C_2H_4(g) \longrightarrow C_2H_6 + 2Ni$$
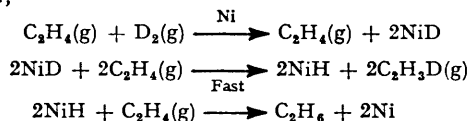
This is the experimental observation of Turkevich. The suggestion has been made (Eyring, see Part I; Eley, *Quart. Rev.*, 1949, **3**, 209) that the ethane formed initially is produced by the decomposition of ethylene on the catalyst, the hydrogen adsorbed then reacting with ethylene. This cannot be true, however, because the ethane formed is far in excess of that which could be produced from the decomposition reaction on the small surface area of the nickel wire catalyst.

CHEMISTRY DEPARTMENT,
    UNIVERSITY OF LONDON, KING'S COLLEGE.