

THE KINETICS OF THE CATALYTIC HYDROGENATION OF ETHYLENE WITH NICKEL. (II)

Reaction at High Temperatures.

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Though it has been observed that the kinetics of the hydrogenation of ethylene at high temperatures (100° – $200^{\circ}\text{C}.$) is apparently simple, the reaction being frequently reported to be nearly second order¹⁾, yet the mechanism of the reaction can not be decided, because a simple relation may be variously interpreted. In the present research the kinetics in the temperature range 99° – $165^{\circ}\text{C}.$ was investigated with nickel catalyst and the results obtained were explained according to the reaction mechanism already proposed at low temperatures²⁾.

Experimental.

The gases used were prepared in the same way as in the preceding report. The catalyst used was obtained as follows: a nickel filament 30 cm. long and 0.2 mm. thick was sealed in a reaction vessel, heated to dull redness in the air to oxidize its surface, and then reduced with hydrogen at $360^{\circ}\text{C}.$ The catalyst was heated up to $200^{\circ}\text{C}.$ and degassed after every experiment. The temperature of the catalyst was controlled by regulating the electric current on the filament which was made one arm of Wheatstone bridge arrangement. Cooling of the ends of the filament being corrected, the temperature of the main part of the filament was determined from the resistance-temperature curve. The temperature thus determined was taken to be that of the catalyst, as the reaction at the ends of the filament may be neglected.

The apparatus is shown in Fig. 1. A is a reaction chamber which holds 150 c.c., B a reservoir of hydrogen or ethylene of almost the same capacity, C a bulb containing the reaction mixture, D and E capillary mercury manometers, F a trap immersed in dry ice and alcohol, and G a thermostat kept at $30^{\circ} \pm 0.005^{\circ}\text{C}.$

In most of the experiments the partial pressure of one reactant was kept constant as in Report I: the pressure decrease in the reaction chamber due to the reaction was incessantly compensated with frequent supply of hydrogen or ethylene by means of the fine capillary H,

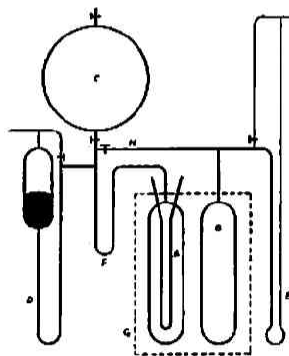


Fig. 1.—Apparatus.

1) Rideal, *J. Chem. Soc.*, 121, 309 (1922); Pease, *J. Am. Chem. Soc.*, 45, 2235 (1923).

2) *Rev. Phys. Chem. Japan*, 9, 119 (1935); 11, 353 (1937).

the manometer D being used as a null-instrument. The rate of reaction was measured from the pressure decrease in the reservoir B by means of the manometer E. An example of the data is given in Table I.

Table I.

Expt. No. 1.

Reac. temp., 117°C. H_2 , 72.5 mm. C_2H_4 , 50.1 mm.

Constant hydrogen pressure.

Time in min.	Press. in the reservoir B in mm.	Time in min.	Press. in the reservoir B in mm.
0	218.3	65.0	190.5
3.2	216.9	69.0	189.5
6.5	215.0	72.8	188.2
10.8	212.9	81.3	185.8
13.9	211.6	86.0	184.8
17.9	209.2	95.0	182.4
20.3	208.3	104.1	181.0
24.2	206.7	108.5	179.3
28.2	204.8	115.0	178.4
32.3	203.2	126.5	176.6
35.5	201.6	135.0	175.2
38.9	200.4	144.8	174.0
43.5	198.2	156.2	172.7
47.5	196.9	168.5	171.6
51.3	195.4	182.3	170.4
56.5	193.5	210	168.8
61.5	191.8	final	167.1

Results.

Activity of the Catalyst:—At low temperatures, as reported in the preceding paper, the activity of the catalyst kept fairly constant inspite of repeated reactions, while at high temperatures it slowly decreased. This decrease could not be prevented even by protecting the catalyst against poisonous vapours by employing a trap, and so it was supposed that heating of the catalyst was the cause. Accordingly, the comparison among the results obtained under different experimental conditions required the correction of the changes of catalytic activity.

Reaction at Constant Hydrogen Pressure:—The experiments at constant pressure of hydrogen are given in Table II. Expts. 1, 3, and 5 were carried out under the same condition and Expts. 6, 8, 10, and 12 were also done under the same condition in order to correct the change of catalytic activity. The numeral of the catalyst denotes the number of renewed reduction. Some of the reaction curves are shown in Fig. 2.

Table II.
Experiments at constant hydrogen pressure.

Catalyst No.	Expt. No.	Reac. temp. (°C)	Initial press. (mm.)		$t_{1/2}$ (min.)	k_1 (min. ⁻¹)		k_2 (mm. ⁻¹)
			H ₂	C ₂ H ₄		Observed	Corrected*	
I	1	117	72.5	50.1	58.9	0.0188	0.0186	0.0163
"	2	144	72.5	50.1		0.0188	0.0187	0.00592
"	3	117	72.4	49.9	59.5	0.0217	0.0217	0.0236
"	4	165	71.7	49.5		0.0177	0.0182	0.00212
"	5	117	73.1	50.5	62.8	0.0178	0.0188	0.0168
I	6	117	69.1	46.5	49.1	0.0266	0.0255	0.0258
"	7	117	9.9	46.5		0.00491	0.00480	0.0194
"	8	117	68.5	47.0	51.2	0.0204	0.0204	0.0166
"	9	117	160.4	46.8		0.0551	0.0527	0.0178
"	10	117	68.9	46.7	54.2	0.0249	0.0264	0.0278
"	11	144	159.8	47.1		0.0457	0.0507	0.00624
"	12	117	68.2	47.2	59.4	0.0206	0.0239	0.0186

* The corrected values of Expts. 1-5 and 6-12 were obtained, assuming that the catalytic activity of each experiment was the same as that of Expts. 3 and 8 respectively.

The reaction was approximately first order at 165°C., while at lower temperatures the order of reaction apparently became lower. In general, the rate of reaction could be represented by the following formula:

$$-\frac{dp}{dt} = k_1 \frac{p - p_f}{1 + k_2(p - p_f)} \quad (1)$$

where p is the pressure of the gas reservoir B in Fig. 1, p_f its final pressure, and k_1 and k_2 constants. The higher the temperature, the smaller k_2 , and the equation approaches that of the first order reaction. That the equation is applicable to each curve is

justified by the fact (Figs. 3 and 4) that a linear relation holds between $\frac{1}{t} \ln \frac{p_0 - p_f}{p - p_f}$ and $\frac{p_0 - p}{p - p_f}$, as may be expected from the integrated form of equation (1):

$$\ln \frac{p_0 - p_f}{p - p_f} + k_2(p_0 - p) = k_1 t,$$

where p_0 is the value of p at $t=0$.

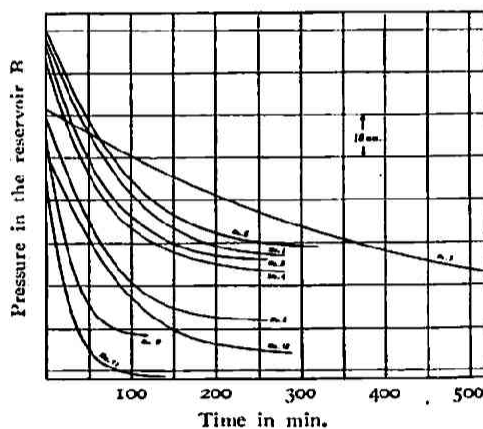


Fig. 2.—Reaction curves at constant pressure of hydrogen.

Initial pressures: No. 1, 218.3 mm.; No. 2, 227.1 mm.; No. 4, 263.5 mm.; No. 5, 240.1 mm.; No. 6, 219.5 mm.; No. 7, 151.5 mm.; No. 9, 285.0 mm.; No. 11, 295.0 mm.; No. 12, 201.2 mm.

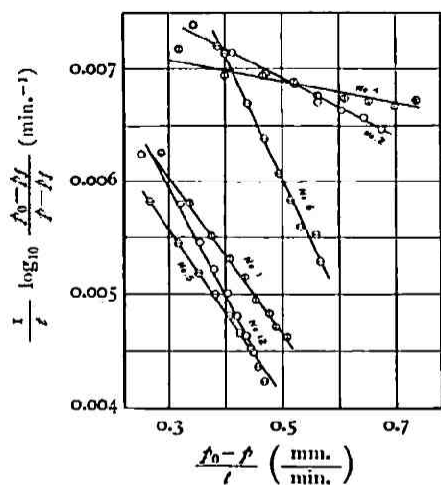


Fig. 3.

From the intercept with the axis and the inclination of the straight line, constants k_1 and k_2 were calculated. k_1 thus obtained, however, had to be corrected for comparison with respect to activity of the catalyst, using $t_{1/2}$ (time of half change) in Table II³⁾. As seen in the table, the corrected value

k_1 is roughly unaffected by change of the temperature, but it varies approximately in proportion to the pressure of hydrogen as in Fig. 5. On the other hand, k_2 becomes markedly smaller with the rise of temperature, but it remains fairly constant when the pressure of hydrogen has been varied as seen in Table II.

Reaction at Constant Ethylene Pressure:—The experiments at constant ethylene pressure are given in Table III.

The reaction curves are shown in Fig. 6.

The rates at constant ethylene pressures could be simply expressed as of the first order reaction thus:

$$-\frac{dp}{dt} = k_3(p - p_f). \quad (2)$$

This was ascertained from its integrated form,

$$\ln \frac{p_0 - p_f}{p - p_f} = k_3 t,$$

as shown in Fig. 7.

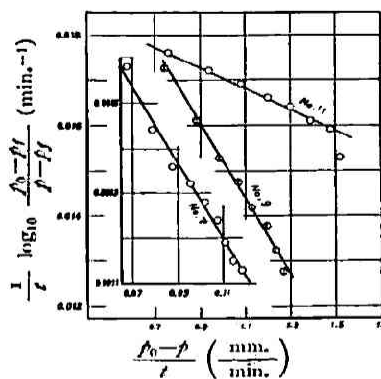


Fig. 4.

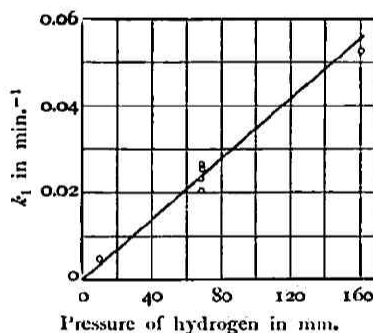


Fig. 5.

3) A slight variation in the inclination of the straight line leads to large difference in the value k_1 and so the catalytic activity was not corrected directly by k_1 .

The constant k_2 obtained from the slope of the straight line was also corrected with respect to the activity of the catalyst. As seen in Table II, k_2 increases with the rise of temperature, but its relation to the pressure of ethylene is not simple, which will be discussed later.

Effect of the Pretreatment of the Catalyst with the Reactants:—Whether the adsorption of any reactant on the catalyst prior to the reaction had any effect

Initial pressures: No. 13, 185.3 mm.; No. 14, 190.1 mm.; No. 16, 189.9 mm.; No. 18, 210.5 mm.; No. 19, 198.1 mm.; No. 20, 243.3 mm.; No. 22, 139.0 mm.; No. 23, 192.6 mm.

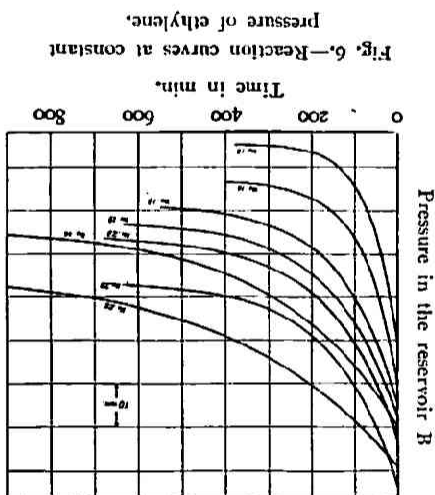


Fig. 6.—Reaction curves at constant pressure of ethylene.

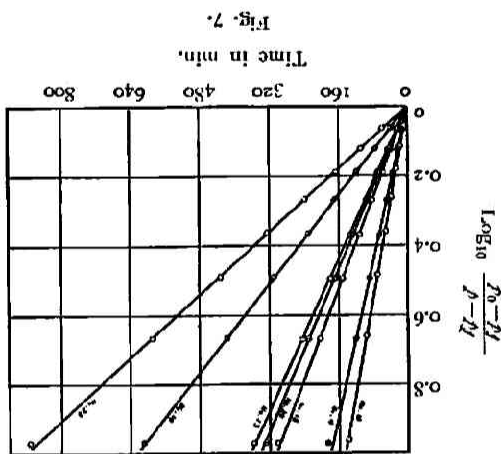


Fig. 7.

Catalyst No.	Expt. No.	Reac. temp. (°C)	Initial press. (mm.)	C_2H_4	Observed	Corrected
I	13	117	45.3	51.9	0.00344	0.00300
"	14	99	45.0	51.5	0.00159	0.00141
"	15	117	45.4	52.0	0.00330	0.00300
"	16	144	45.6	52.2	0.00559	0.00532
"	17	117	45.0	51.5	0.00300	0.00300
"	18	165	45.1	51.6	0.00697	0.00710
"	19	117	44.9	51.4	0.00289	0.00300
"	20	117	45.2	129.4	0.00294	0.00284
"	21	117	45.0	51.5	0.00284	0.00284
"	22	117	45.5	10.2	0.00113	0.00115
"	23	117	45.6	51.3	0.00276	0.00284

Experiments at constant ethylene pressure.

Table III.

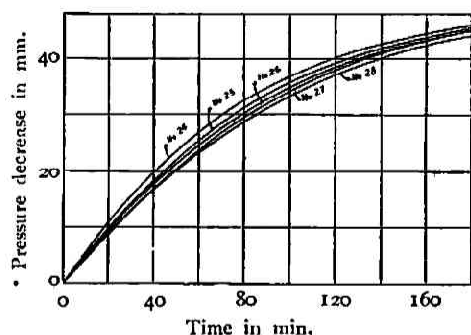


Fig. 8.—Experiments on the pretreatment of the catalyst.

Initial pressures: No. 24, 64.1 mm. H_2 +46.7 mm. C_2H_4 ; No. 25, 63.5 mm. H_2 +46.8 mm. C_2H_4 ; No. 26, 64.3 mm. H_2 +47.5 mm. C_2H_4 ; No. 27, 63.3 mm. H_2 +47.9 mm. C_2H_4 ; No. 28, 63.9 mm. H_2 +47.8 mm. C_2H_4 .

contact with the catalyst. The third experiment was similar to the first. In this way a series of experiments were carried out.

As seen in Fig. 8, there is, as a whole, a steady decrease in the rate of reaction due to that in activity of the catalyst. No specific influence of the pretreatment, however, is noticeable: when the fall of activity is taken into account, all the curves will coincide with each other at the initial part, while the effect of the pretreatment, if any, is expected to appear in the initial stage of the reaction. It may be admitted, therefore, that under the present experimental conditions the rate of reaction is not affected by the pretreatment of the catalyst.

The Effect of the Reaction Product:—To examine whether ethane, the product, participated in the rate of reaction, a number of experiments were carried out with the reactants preliminarily mixed with ethane. The results obtained are

Table IV.

Experiments with added ethane (constant ethylene pressure).
Catalyst, No. V. Reac. temp., 117°C.

Expt. No.	Initial pressure (mm.)			$k_3 \cdot 0.4343$ (min. ⁻¹)
	H_2	C_2H_4	C_2H_6	
29	50.3	50.8		0.00389
30	50.1	50.5	41.3	0.00383
31	50.6	50.6		0.00380
32	49.9	50.3	95.1	0.00377
33	50.5	50.9		0.00371

given in Table IV, which indicates that ethane has no influence on the rate of reaction as in the reaction at low temperatures.

Discussion.

Since the concentration of ethane is not related to the rate of reaction, only that of ethylene can be regarded as variable in the gaseous phase when the pressure of hydrogen is kept constant. Hence, equation (1) obtained experimentally may be written as follows:

$$\left(\frac{dx}{dt}\right)_{p_{H_2}=\text{const.}} = k_1 \frac{p_{C_2H_4}}{1 + k_2 p_{C_2H_4}} \quad (3)$$

Similarly, equation (2) becomes

$$\left(\frac{dx}{dt}\right)_{p_{C_2H_4}=\text{const.}} = k_3 p_{H_2} \quad (4)$$

Consequently, the rate of reaction may be generally given by

$$\frac{dx}{dt} = k_4 \frac{p_{H_2} p_{C_2H_4}}{1 + k_2 p_{C_2H_4}} \quad (5)^4$$

On the other hand, it was shown in the preceding paper that the hydrogenation took place presumably by the combination of both reactants adsorbed on the active surface of the catalyst and that the rate of the surface reaction determined the whole reaction rate which could be approximately represented by the following formula obtained by applying Langmuir's isotherm to the adsorption of both competing reactants:

$$\frac{dx}{dt} = k \frac{a p_{H_2} \cdot \beta p_{C_2H_4}}{(1 + a p_{H_2} + \beta p_{C_2H_4})^2} \quad (6)$$

where a and β are the adsorption coefficients of hydrogen and ethylene respectively.

It seems probable that the reaction at high temperatures is brought forth according to the same mechanism as at low temperatures⁵⁾. The rate of reaction at high temperatures is again considered to be determined by that of the surface reaction between the adsorbed reactants. For it is deduced from the independence

4) A similar relation was derived from the work of zur Strassen (*Z. physik. Chem. (A)*, 169, 81 (1934); Schwab, *ibid.*, 171, 421 (1935)).

5) In the present experiments, a filament catalyst was employed in place of the powder form in the preceding work. But in the preliminary experiments at room temperature, similar results were obtained as already reported with this filament catalyst. So the form of the catalyst makes no difference.

of the reaction rate of both the pretreatment of the catalyst and the addition of ethane to the reaction mixture that the rate of reaction is not influenced by the rate of adsorption of the reactants and that of desorption of the product. It may be concluded, therefore, that the difference between the kinetic expression obtained at high temperatures (5) and that at low temperatures (6) should be ascribed merely to decrease in the adsorbed amount of the reactants due to rise of temperature. In fact, assuming that $\alpha p_{H_2} \ll 1$ and $\beta p_{C_2H_4} < 1$ in equation (6), we obtain approximately

$$\frac{dx}{dt} = k\alpha\beta \frac{p_{H_2}p_{C_2H_4}}{1 + 2\beta p_{C_2H_4}}, \quad (7)$$

which is of the same form as equation (5).

Hence, the constants in equation (3) should satisfy the following relations:

$$k_1 = k\alpha\beta p_{H_2}, \quad (8)$$

and $k_2 = 2\beta. \quad (9)$

Of these two, the former holds, in practice, as shown in Fig. 5, and it is in concordance with the latter that k_2 has practically no relation to the pressure of hydrogen, as seen in Table II.

The constant k_3 may be similarly given from equation (7), but to this case it is adequate to apply the following relation,

$$k_3 = k \frac{\alpha\beta p_{C_2H_4}}{(1 + \beta p_{C_2H_4})^2}, \quad (10)$$

which is obtained from the original equation (6), so that it may be applicable to the experiments at higher pressures of ethylene. To verify this relation, β was calculated from the mean value of k_2 in Table II by the relation (9), and substituted in equation (10); a theoretical curve for the relation between k_3 and the pressure of ethylene was drawn so as to coincide with the experimental value of k_3 obtained at the highest pressure of ethylene; as seen in Fig. 9, the curve represents the actual dependence of k_3 on the ethylene pressure approximately.

The relation between k_2 and temperature in Table II can be considered to show the dependence of the adsorption coefficient β on temperature from the relation (9). Let Q_R represent the adsorption heat of ethylene per mole, then a well-known relation holds:

$$\beta = \beta_0 e^{Q_R/RT},$$

where β_0 is a constant, R the gas constant and T the absolute temperature.

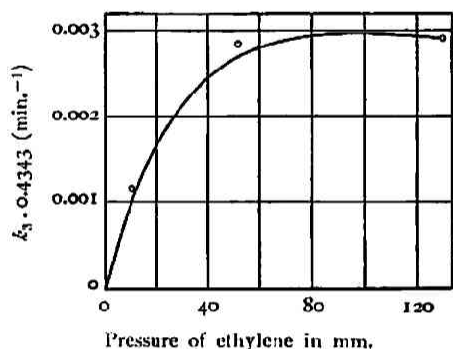
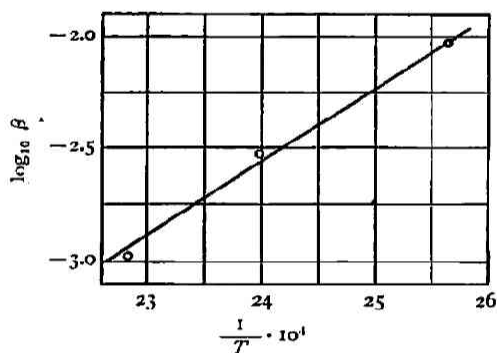


Fig. 9.

Fig. 10.—The mean value of $\log_{10} \beta$ obtained from Expts. 1, 3 and 5 is indicated by $\odot$.

Calculating β from k_2 in Table II, and plotting $\log \beta$ against $1/T$ as shown in Fig. 10, Q_H was obtained thus:

$$Q_H = 14.9 \text{ kcal. per mole.}$$

On the other hand, as seen from Table II, the temperature coefficient of k_1 is nearly zero, so let E and Q_H represent the activation heat of the surface reaction and the adsorption heat of hydrogen respectively, then the following relation is easily obtained,

$$E \sim Q_H + Q_E,$$

taking equation (8) into consideration⁶⁾.

Although the adsorption heat of hydrogen may be small from the relation $\alpha < \beta$, yet the heat of activation will be no less than 15 kcal.—the heat of adsorption of ethylene. The value must be, therefore, far greater than the apparent energy which has been frequently reported to be only several kcal.

Summary.

The kinetics of the hydrogenation of ethylene with nickel catalyst has been investigated statically in the temperature range 99°–165°C.

The results agree with those obtained previously at lower temperatures in the following fact that the rate of reaction is practically independent of ethane and the pretreatment of the catalyst with any reactant gas.

The rate of reaction is represented by

$$\frac{dx}{dt} = k_1 \frac{p_{C_2H_4}}{1 + k_2 p_{C_2H_4}}.$$

6) Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems." p. 352 (1933).

when the pressure of hydrogen is kept constant, and by

$$\frac{dx}{dt} = k_3 p_{H_2},$$

when the pressure of ethylene is kept constant. These expressions are somewhat different from those suggested theoretically at lower temperatures. The difference is, however, ascribed only to decrease in the concentrations of the adsorbed reactants resulting from the rise of temperature, inasmuch as it is believed that the reaction mechanism is identical regardless of temperature. The dependence of the constants of the rate equations upon the temperature and pressures of the reactants justifies the above described interpretation.

From the temperature coefficient of the constant k_2 , the heat of adsorption of ethylene is found to be about 15 kcals. per mole. The temperature independence of the constant k_1 indicates that the true heat of activation for the reaction is roughly as large as the sum of the adsorption heats of both reactants.

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