

## THE KINETICS OF THE HYDROGENATION OF PROPYLENE ON A NICKEL CATALYST.\*

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In the two preceding reports on the hydrogenation of ethylene some conclusions were drawn about the rate-determining step of the hydrogenation, the reaction mechanism on the catalyst surface, and magnitudes of the heats of activation and adsorption.<sup>1),2)</sup> It seemed then desirable to carry out a similar study with propylene and to compare the results with those obtained with ethylene for such comparison would give a further support to the conclusions obtained with ethylene and also some general informations about the hydrogenation of gaseous olefines.

In the present work, the rate of hydrogenation of propylene was first investigated under various experimental conditions as little had yet been known about its kinetics. And then the relative rates of hydrogenation of propylene and ethylene were determined at various temperatures. Some experiments with mixtures of propylene and ethylene were also carried out.

### Experimental.

Ethylene and hydrogen were prepared in the same way as described in the previous paper.<sup>1)</sup> Propylene was generated by dehydration of isopropyl alcohol in the same apparatus as used for ethylene and was purified by repeated fractional distillation.

A nickel filament 0.1 mm. in diameter and 40 cm. long was sealed in the reaction vessel as the catalyst. Its surface was activated by oxidation and reduction as described previously, the activity being controlled by an appropriate heat treatment. Temperature of the catalyst was determined by measuring its resistance in a Wheatstone bridge as before.<sup>2)</sup>

The activity of the catalyst was considerably deteriorated in contact with propylene and so it was desirable to carry out experiments at low pressure. For the purpose of comparison with the hydrogenation of ethylene previously investigated, however, it was undesirable to lower the pressure far more than in the

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\* A preliminary report on these experiments was presented at Tokyo meeting of the Chemical Society of Japan, April 1939.

1) O. Toyama, *This Journal*, 11, 353 (1937).

2) O. Toyama, *ibid.*, 12, 115 (1938).

case of ethylene. Taking these circumstances into consideration, the initial pressure of propylene was reduced below 1 cm. Hg., i. e. to a few tenths of that of ethylene in the previous experiments.

The apparatus is shown in Fig. 1. The reaction chamber was a cylindrical

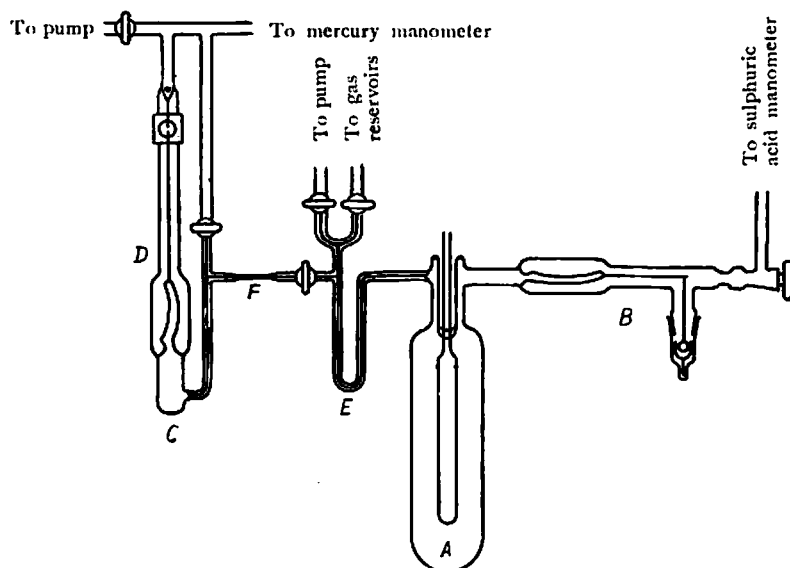


Fig. 1—Apparatus: A, reaction chamber; B and D, Bourdon gauges; C, gas reservoir; E, trap; F, capillary leak.

glass vessel of 200 c.c. capacity. The glass Bourdon gauge attached to it had a somewhat higher sensitivity than any other ordinary one, variation in pressure being converted into the rotation of a mirror.<sup>3)</sup> Fig. 2 shows a calibration curve for the gauge obtained by the comparison with a sulphuric acid manometer.

In order to get a clearer image of the kinetics, most of the experiments were carried out at constant pressure of either hydrogen or propylene as in the previous studies: the

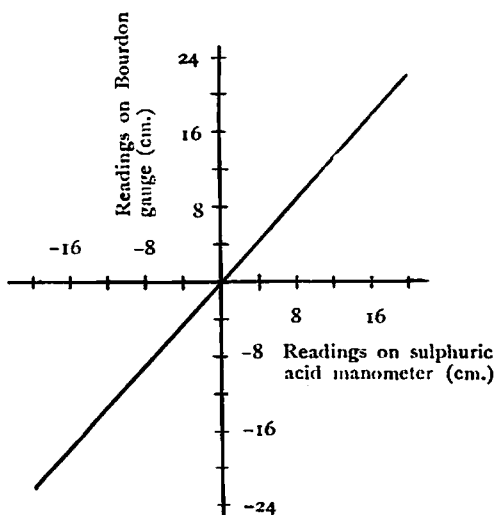


Fig. 2—A calibration curve for Bourdon gauge B.

3) The device is similar in principle to that described by S. G. Foord (*J. Sci. Instr.* 11, 126 (1934)).

fall in pressure due to the reaction was incessantly compensated by frequent supply of either hydrogen or propylene from the reservoir C which contained about 20 c.c. of gas at a pressure about 10 cm. Hg. The gauge B, in this case, was used as a null-instrument to keep the pressure in the reaction chamber constant and the rate of reaction was calculated from the pressure decrease in the reservoir C recorded on a Bourdon gauge D.<sup>4)</sup>

The hydrogenation always proceeded to the end, i.e. the observed total pressure change agreed with that calculated within an error. Analysis of the product showed that propylene was hydrogenated exclusively to propane.

The procedure for taking a run was as follows: after the reaction chamber was well evacuated, a mixture of the reactants was introduced; the catalyst was then heated up to a required temperature and the progress of reaction was recorded. In the course of the reaction, the temperature of the catalyst was kept constant by adjusting the heating current so as to make its resistance in a Wheatstone bridge constant.

In the experiments the reaction vessel was kept at 25°C. in a water-bath and the reservoir C in ice. The trap E was immersed in a bath of dry ice and alcohol with the object of protecting the catalyst against poisonous vapours.

## Results.

### The Poisoning Action of Propylene.

It was already found in the study of the hydrogenation of ethylene that the activity of catalyst in contact with ethylene was gradually deteriorated.<sup>2)</sup> Propylene exerted even a greater poisoning action in spite of repeated purification. The poisoning by propylene as well as that by ethylene was more remarkable at high temperatures. The presence of hydrogen, on the other hand, protected the catalyst from such poisoning to a great extent. The poisoning therefore seems to have resulted from slow decomposition or polymerisation of the olefines on the active surface of the catalyst. The greater poisoning action of propylene would be attributed to its less stability.

In the experiments carried out at constant pressure of propylene in the neighbourhood of 100°C., a marked falling off of the activity of the catalyst was observed during the reaction. Undoubtedly propylene deteriorated the catalyst as hydrogen playing a rôle of protector was used up with the progress of reaction.

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4) In the calculation the initial concentrations of the reactants were also represented in mm. Hg in the reservoir C for convenience.

Consequently, any exact data about the kinetics could not be obtained in these experiments. The kinetics of reaction, therefore, was determined chiefly from the experiments at constant pressure of hydrogen, in which the falling off of the activity of the catalyst during the reaction was minimised.

### The Hydrogenation of Propylene at Constant Pressure of Hydrogen.

In the temperature range 25—178°C., propylene gave the reaction curves which closely resembled those obtained previously with ethylene: at low temperatures the reaction curve has a slightly autocatalytic form and it approaches that of the first order with rise of temperature. For example, Figs. 3 and 4 show some of the reaction curves which are to be compared with Figs. 5 and 8 in the first report<sup>1)</sup> and Fig. 3 in the second report<sup>2)</sup> on the hydrogenation of ethylene.

It seems, therefore, quite obvious that the mechanism of the reaction is

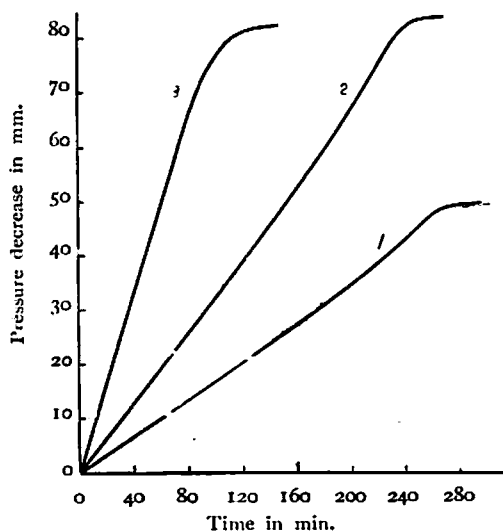


Fig. 3—Experiments at constant hydrogen pressure:

- 1, 49.1 mm.  $C_3H_6$ +43.8 mm.  $H_2$  at 25°C.;
- 2, 84.8 mm.  $C_3H_6$ +88.3 mm.  $H_2$  at 25°C.;
- 3, 83.0 mm.  $C_3H_6$ +88.0 mm.  $H_2$  at 51°C.

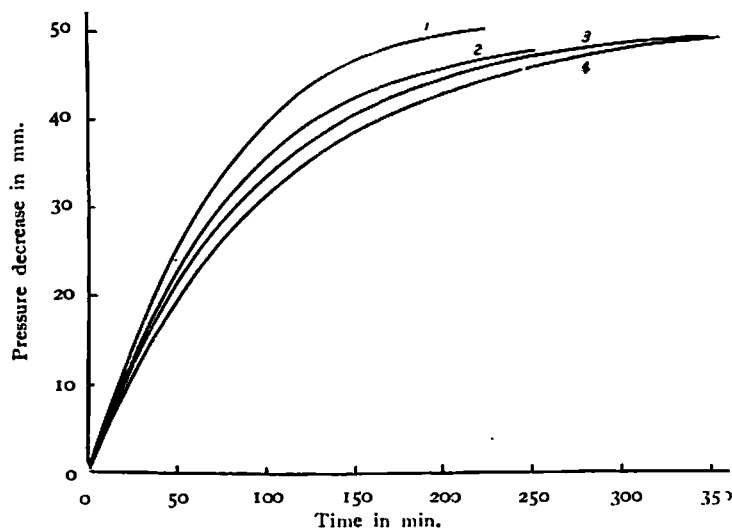


Fig. 4—Experiments at constant hydrogen pressure:

- 1, 50.5 mm.  $C_3H_6$ +80.3 mm.  $H_2$  at 98°C.; 2, 49.9 mm.  $C_3H_6$ +80.0 mm.  $H_2$  at 120°C.;
- 3, 49.8 mm.  $C_3H_6$ +80.1 mm.  $H_2$  at 141°C.; 4, 50.1 mm.  $C_3H_6$ +79.5 mm.  $H_2$  at 160°C.

identical with that of the hydrogenation of ethylene. Accordingly the reaction curves are to be explained by the following theoretical formula similar to that in the case of ethylene<sup>1)</sup>:

$$\frac{dp_{C_3H_6}}{dt} = k \frac{\alpha p_{H_2} \cdot \beta^2 p_{C_3H_6}}{(1 + \alpha p_{H_2} + \beta p_{C_3H_6})^2} \quad (1)$$

where  $\alpha$  and  $\beta$  are adsorption coefficients for hydrogen and propylene respectively. The autocatalytic curves at low temperatures could not be otherwise adequately explained. The coincidence between the theory and the results, however, has been found to be more or less qualitative at these low temperatures. This is probably because various factors such as the inhomogeneity of the catalyst surface, the interaction between the adsorbed molecules, the difference in the molecular volumes of the two reactants etc have been neglected in the derivation of the theoretical formula. Namely, the concentrations of the adsorbed reactants might be so high at low temperatures that these factors should have been taken into consideration.

At higher temperatures, as already experienced in the case of ethylene, the kinetics of the reaction could be dealt with more quantitatively: in the neighbourhood of 100°C., the rate of reaction at constant pressure of hydrogen was represented by

$$\frac{dp_{C_3H_6}}{dt} = k_1 \frac{p_{C_3H_6}}{1 + k_2 p_{C_3H_6}} \quad (2)$$

which is derived from formula (1) taking into account that adsorption is small at these temperatures<sup>2)</sup>. Some examples showing the validity of equation (2) are given in Fig. 5, which shows that there holds in general a linear relation between the two quantities in the integrated form of equation (2) as it is required. Constants  $k_1$  and  $k_2$  determined from such graphical plots are given in Table I, where all the figures are tabulated in the order of experiments. The experiments

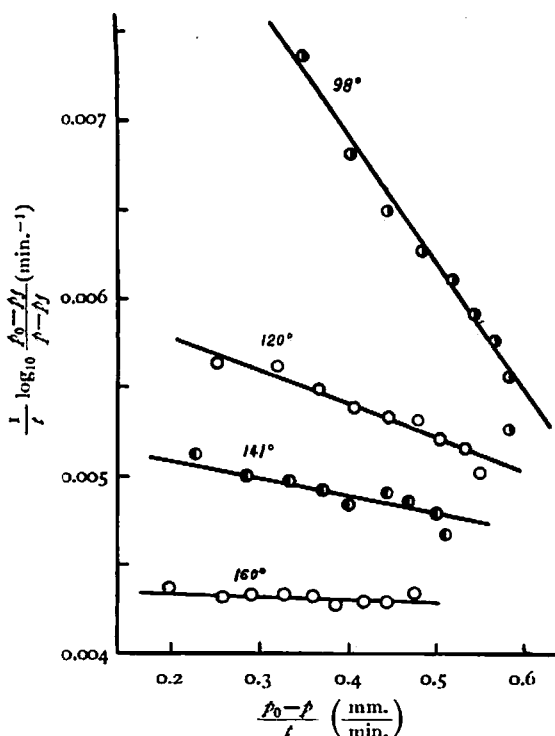


Fig. 5—The relation between  $\frac{1}{4} \log_{10} \frac{p_0 - p_f}{p - p_f}$  and  $\frac{p_0 - p}{t}$ . ( $p_0$ , initial pressure;  $p_f$ , final pressure;  $p$ , pressure at time  $t$ .)

carried out at temperatures 160 and 178°C. are lacking in the value of  $k_2$ , because the values could not be determined in these cases,  $k_2$  being so small that the reaction was practically first order as shown in Table II. Throughout the

Table I.

Values of constants  $k_1$  and  $k_2$  obtained from the experiments at constant hydrogen pressure.

Initial pressures (mm.)		Temp. (°C.)	$k_1$ (min. <sup>-1</sup> )	$k_2$ (mm. <sup>-1</sup> )
C <sub>3</sub> H <sub>6</sub>	H <sub>2</sub>			
50.5	80.3	98	0.0221	0.0152
49.9	80.0	120	0.0142	0.00434
49.8	80.1	141	0.0119	0.00149
50.1	79.5	160	0.00995	
50.3	79.8	98	0.0193	0.0109
50.4	40.2	98	0.0114	0.0137
50.2	39.7	120	0.0801	0.00387
49.9	40.3	141	0.00640	0.00184
50.4	40.0	178	0.02366	
49.7	79.9	98	0.0210	0.0126

Table II.

The reaction at constant pressure of hydrogen at 178°C.

Decrease in pressure (mm.)	Time (min.)	0.4343 $k_1$ (min. <sup>-1</sup> )
5	29	0.00156
10	61	0.00157
15	97	0.00158
20	138	0.00159
25	186	0.00160
30	247	0.00159
35	323	0.00159
40	428	0.00160
45	602	0.00160

series of experiments given in Table I, the activity of the catalyst was kept approximately constant by heating the catalyst in hydrogen at 200°C. for an hour after each experiment. The constancy of the activity is seen by comparing the values of  $k_1$  obtained under similar experimental conditions.

The constants  $k_1$  and  $k_2$  are related with the true rate constant and adsorption coefficients as follows:<sup>2)</sup>

$$k_1 = k\alpha\beta, \quad (3)$$

$$k_2 = 2\beta, \quad (4)$$

where  $k$  is the true rate constant and  $\alpha$  the pressure of hydrogen. It is seen in Table I that the value of  $k_1$  is nearly doubled when the hydrogen pressure is doubled, satisfying the proportionality which is required by equation (3). The temperature dependence of  $k_1$  and  $k_2$  is shown in Fig. 6, from which, according to equations (3) and (4), the following relations are obtained:

$$Q_P \simeq 15 \text{ kcal.}, \quad (5)$$

$$E_P \simeq Q_H + Q_P - 4 \text{ kcal.},$$

where  $E_P$  is the true heat of activation of the reaction and  $Q_H$  and  $Q_P$  are heats of adsorption of hydrogen and propylene respectively. The corresponding relations previously obtained for ethylene are as follows:

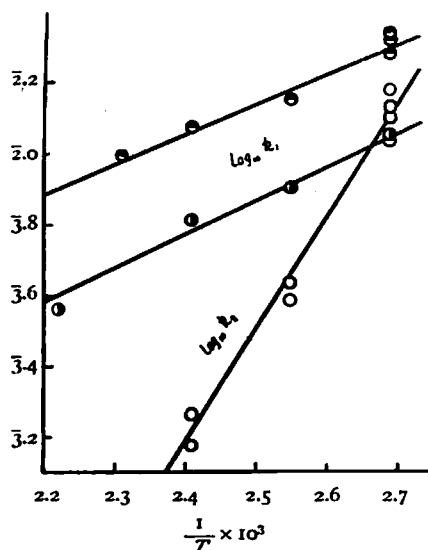


Fig. 6—The temperature dependence of the values of  $k_1$  and  $k_2$ .

kcal. for ethylene, active charcoal impregnated with 1% nickel being used as a catalyst; according to the latter investigator, the apparent heat of activation for propylene is 6 kcal. and that for ethylene is 3.2 kcal.

The effect of the reaction product on the rate of reaction was investigated in the following way: propylene was hydrogenated to propane with excessive quantity of hydrogen in the reaction chamber; to the mixture of propane and hydrogen thus obtained in the reaction vessel propylene was added and the rate of reaction was measured at a constant pressure of hydrogen; the initial rate thus determined was compared with that in the absence of propane. The results given in Table III show that the reaction product has little effect on the rate of reaction

Table III.

Experiments with added propane.

Initial pressures (mm.)			Temp. (°C.)	Initial rate (mm./min.)
H <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>		
81.0	80.6	81.1	25	0.0335
81.5	81.3		25	0.0321
82.2	80.7	131.6	51	0.0851
81.9	80.5		51	0.0839

5) C. Schuster, *Trans. Farad. Soc.*, 26, 407 (1932).

6) G. H. Twigg, *ibid.*, 35, 934 (1939).

$$Q_E \approx 15 \text{ kcal.}, \quad (6)$$

$$E_E \sim Q_H + Q_E,$$

where  $E_E$  is the true heat of activation in the hydrogenation of ethylene.<sup>5)</sup> Comparison between relations (5) and (6) shows that the true heat of activation for propylene is lower than that for ethylene by about 4 kcal. since the adsorption heats of both olefines are nearly equal. The result is not in agreement with the earlier data obtained by Schuster<sup>5)</sup>, but it is qualitatively compatible with the result lately obtained by Twigg<sup>6)</sup>: the former investigator found as the apparent heats of activation 4.8 kcal. for propylene and 3.6

as in the case of ethylene.<sup>7)</sup>

### The Hydrogenation of Propylene at Constant Pressure of Propylene.

As already mentioned, the experiment at constant pressure of propylene was inadequate for the investigation of the kinetics, since the activity of the catalyst fell off during the reaction. The general feature of the reaction, however, will be seen in Fig. 7, in which three experiments carried out successively at 51, 98

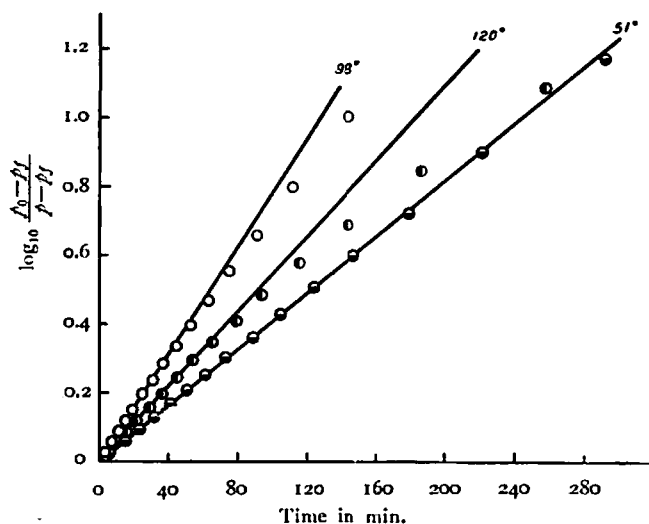


Fig. 7—Experiments at constant propylene pressure:  
51°C.—curve, 79.8 mm.  $C_3H_6$ +80.5 mm.  $H_2$ ; 98°C.—curve, 81.1 mm.  
 $C_3H_6$ +80.2 mm.  $H_2$ ; 120°C.—curve, 80.5 mm.  $C_3H_6$ +80.1 mm.  $H_2$ .

and 120°C. are given for examples. The plots for the experiment at 51°C. lie on a straight line, i.e. the reaction is first order, while the other plots show deviations from such linearity. The markedly slow rate at 120°C., however, indicates that the activity of the catalyst considerably fell off in the preceding experiment at 98°C. Accordingly, the catalyst must have suffered a still greater deterioration in the experiment at 120°C. It may be inferred, therefore, that the reaction remains to be first order even at temperatures above 100°C., as in the case of ethylene, were it not for the deterioration of the activity of catalyst during the reaction. And this is also what is expected from rate formula (1).<sup>2)</sup>

7) In the previous papers diffusion processes in the gaseous phase were considered to be sufficiently rapid and to have no influence on the rate of hydrogenation, since the reaction was in general allowed to take place very slowly. The fact that addition of propane or ethane<sup>1),2)</sup> does not disturb the rate of hydrogenation may be taken for a proof of validity of such consideration.



**Relative Rates of Hydrogenation of Propylene and Ethylene.**

Table IV shows the rates of hydrogenation of propylene and ethylene measured alternately at various temperatures. In these experiments only the

Table IV.

Comparison between the rates of hydrogenation of  $C_2H_4$  and  $C_3H_6$ .

Initial pressures (mm.)			Temp. (°C.)	Initial rate (mm./min.)	Ratio of rates
$C_2H_4$	$C_3H_6$	$H_2$			
70.5		71.3	25	0.0556	
	70.1	71.9	25	0.0385	1.44
71.2		71.7	51	0.170	
	72.2	72.0	51	0.103	1.65
70.9		71.5	98	0.575	
	71.0	70.8	98	0.189	3.04
71.7		71.1	141	0.562	
	71.5	72.1	141	0.192	2.93
72.3		71.3	160	0.455	
	70.8	71.3	178	0.0676	4.33*

\* Calculated as the ratio at 160°C. by using an interpolated value for the rate of  $C_3H_6$ .

initial rates were determined with intent to avoid any possible change in the activity of the catalyst. As seen in the table, propylene is hydrogenated more slowly than ethylene, the difference in the rates increasing with rise of temperature. The temperature dependence of these initial rates is shown in Fig. 8, where logarithms of the rates are plotted against the reciprocals of absolute temperatures. Both curves in the figure show maxima at about 110°C., though less sharp in the case of ethylene.

The appearance of such a maximum in rate was first observed by Rideal<sup>8)</sup> in an investigation of the hydrogenation of ethylene on nickel and it was later discussed

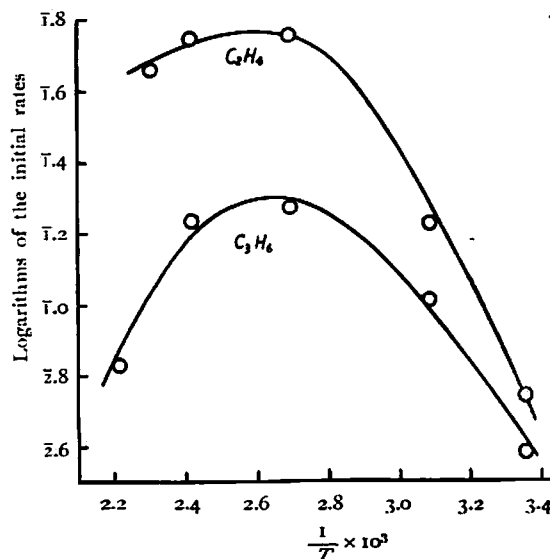


Fig. 8—The temperature dependence of the initial rates of the hydrogenation of  $C_2H_4$  and  $C_3H_6$ .

8) E. K. Rideal, *J. Chem. Soc.*, 121, 309 (1922).

by zur Strassen<sup>9)</sup>. According to zur Strassen, the reaction has a negative temperature coefficient at high temperatures because decrease in the concentrations of the adsorbed reactants with rise of temperature cannot be covered by increase in the rate constant, while at low temperatures, where the catalyst becomes saturated with ethylene and consequently its concentration shows no more temperature dependence, the temperature coefficient of reaction becomes positive. He tacitly considered here the adsorptions of ethylene and hydrogen to exert no influence on each other, as he worked at pressures so low that no clear indication of retarding effect of ethylene was observed. It has been, however, established in the present work and the preceding one that both ethylene and propylene really exert such retarding effects. Therefore, the positive temperature coefficients observed at low temperatures must be explained in somewhat different way from that given by zur Strassen. That is, the temperature coefficient becomes positive at low temperatures not only because the concentration of either of the olefines adsorbed becomes high and insensitive to the temperature change, but also because the adsorption of hydrogen is much hindered by the stronger adsorption of either of the olefines at low temperatures and this retarding action more or less contributes to the temperature coefficient of reaction in the positive direction. As to the negative temperature coefficient observed at high temperatures, the explanation given by zur Strassen is valid since there is practically no discrimination between the two kinds of adsorption of gases with and without mutual displacement at these high temperatures where the gases are adsorbed only in small amounts.

The negative temperature coefficient is not so clearly observed in the hydrogenation of ethylene because in this case the increase in the rate constant with rise of temperature nearly compensates the fall in rate due to diminution in the concentrations of adsorbed molecules as already described (equation (6)). In the hydrogenation of propylene, on the other hand, the energy of activation is somewhat lower and consequently the temperature coefficient is more clearly negative.

It must be pointed out that propylene is hydrogenated rather more slowly than ethylene notwithstanding that the activation energy for propylene is lower<sup>10)</sup>. Similar results were reported by Twigg<sup>6)</sup> too, but without any detailed discussion of the matter. The easiest way of explanation, at first sight, might be that propylene reacts more slowly because it retards the reaction to a greater extent by

9) H. zur Strassen, *Z. physik. Chem.*, A, 169, 81 (1934).

10) Computing from the difference in the activation heats alone, propylene should be hydrogenated at least  $10^2$  times faster than ethylene in the temperature range of the present investigation.

displacing more hydrogen on the catalyst. It is, however, highly improbable that there is any such serious difference in the retarding actions of both olefines judging from the adsorption heats (equations (5) and (6)), though slight difference might arise from the inequality in molecular volumes. In addition to this, the fact that propylene reacts more slowly even at such high temperatures as the retarding actions of both olefines are no more recognized gives a decisive evidence against the view suggested above. Hence, the matter must be explained in some other way.

Let us now write the rate of hydrogenation in the form

$$\frac{dx}{dt} = kAC_H C_o, \quad (7)$$

where  $k$  is the rate constant,  $A$  the area of the active surface of the catalyst,  $C_H$  and  $C_o$  are respectively the concentrations of hydrogen and either of the olefines on the catalyst. The rate constant  $k$  is in turn given by

$$k = \sigma Z e^{-\frac{E}{RT}}, \quad (8)$$

where  $E$  is the activation energy,  $Z$  the number of encounter of the two reacting molecules per unit time, unit area and unit concentrations, and  $\sigma$  the probability factor.

Now the fact that propylene is hydrogenated rather more slowly than ethylene in spite of its lower activation energy must have resulted from a smaller value of the product  $\sigma Z$  in the reaction of propylene, for it has been already established that there cannot be so much difference in the values of  $C$ 's that the difference in the activation energy can be wholly compensated. It is indeed most probable that the hydrogenation of propylene has a much smaller probability factor owing to its methyl group. The values of  $Z$ , on the other hand, may be of the same order of magnitude for both olefines. Hence, it may be concluded that the smaller probability factor in the hydrogenation of propylene is chiefly responsible for the observed fact.

#### The Hydrogenation of a Mixture of Propylene and Ethylene.

The experiments with mixtures of the two olefines were carried out with the object of investigating whether they are hydrogenated with the same relative rates as determined before from separate experiments. The results are given in Fig. 9. The reaction curve obtained at 25°C. shows a slightly autocatalytic form much the same as that already found for the two olefines (see p. 89). This suggests that both olefines are hydrogenated with the rates not so much different at 25°C.,

as may be expected from the rates of separate hydrogenation.

The reaction curve at 98°C., on the other hand, consists of two parts, i.e. a relatively rapid reaction in the initial part is followed by a much slower one. This may be recognized by inspection, but is more clearly seen in Fig. 10: if the two olefines were hydrogenated with the same rate, all the plots in the figure would lie on a straight line as was shown in Fig. 5; the results given in Fig. 10, indicates

that the hydrogenation proceeds in two steps, a rapid process preceding to a

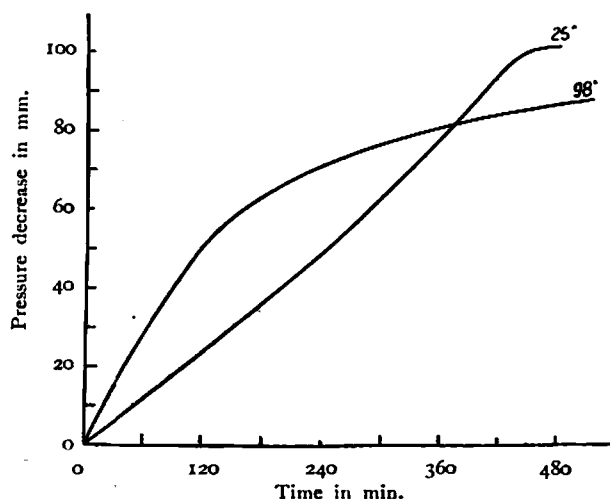


Fig. 9—Experiments with mixtures of  $C_2H_4$  and  $C_3H_6$ :  
25°C.—curve, 51.9 mm.  $C_2H_4$ +49.3 mm.  $C_3H_6$ +50.3 mm.  $H_2$ ;  
98°C.—curve, 53.1 mm.  $C_2H_4$ +50.7 mm.  $C_3H_6$ +49.5 mm.  $H_2$ .  
Time scale for 98°C.—curve is enlarged 4 times.

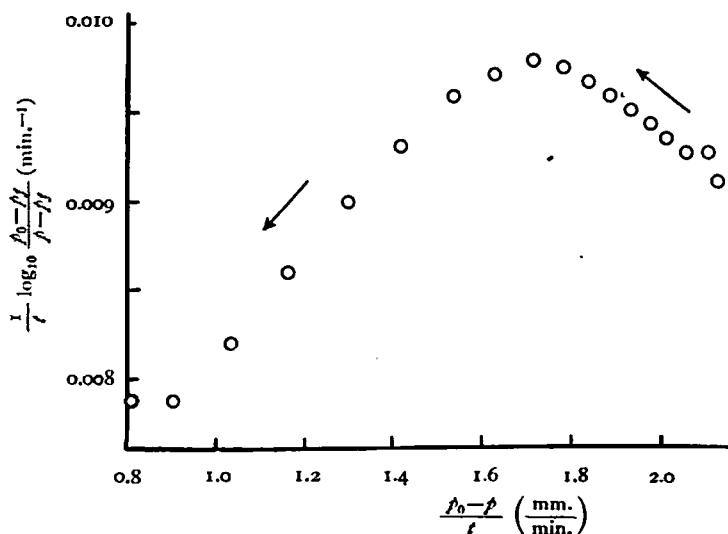


Fig. 10

slower one. It may, therefore, be concluded that ethylene is hydrogenated much faster than propylene at about 100°C. even in the mixture of both olefines as was found in the separate hydrogenation.

There is no sign of any greater retarding action of propylene which was discussed before, or else the hydrogenation of ethylene would be markedly

retarded in the presence of propylene. The results here obtained therefore support the conclusion reached previously.

### Conclusions for the Hydrogenation of Ethylene and Propylene.

It is obvious from the experimental results obtained in this work and previous ones that ethylene and propylene are hydrogenated on nickel with the identical mechanism. Under the experimental conditions in these experiments, the over-all rate of hydrogenation is determined by the addition of hydrogen taking place between the reactants both adsorbed on the catalyst. The kinetics of the reaction shows that the adsorptions of both reactants are not without influence on each other though frequently so believed, and at low temperatures, in fact, the adsorption of hydrogen is hindered by much stronger adsorption of either of the olefines. On the other hand, the adsorptions of ethane and propane, the products of hydrogenation, must be far less in amount since their presence has no influence on the rates of hydrogenation.

The temperature coefficient of the reaction is positive at low temperatures, while at higher temperatures it becomes more or less negative. Consequently, the rate of reaction attains to a maximum at an intermediate temperature. The reversal of the temperature coefficient is mainly caused by the temperature dependence of the adsorption of either of the olefines.

The kinetics of the hydrogenation and its dependence on the temperature is, on the whole, satisfactorily explained by the theoretical formula derived on the basis of the assumptions that hydrogen is added to either of the olefines by a bimolecular process and that the concentration of each reactant on the catalyst is given by Langmuir's adsorption isotherm. At low temperatures the agreement between the theory and the results is more or less qualitative probably because various approximations made in the derivation of the theoretical formula are not fully justified at low temperatures where the concentrations of the reactants on the catalyst are high.

The analysis of the reaction curves obtained at high temperatures shows that the adsorption heats of the two olefines are nearly the same, i.e. about 15 kcal., while the activation heat of the hydrogenation of propylene is lower than that of ethylene by about 4 kcal. Nevertheless, propylene is hydrogenated rather more slowly than ethylene in the present temperature range. This suggests that the probability factor in the hydrogenation of propylene is much smaller than that in the case of ethylene.

It has been frequently believed without any convincing evidence that the hydrogen molecule is dissociated into atoms on a catalyst before it is added to the double bond. The general validity of the theoretical formula above mentioned, however, makes it plausible that molecular hydrogen is added as a whole to the double bond on the catalyst, though possibility of the atomic mechanism cannot entirely be excluded, for a simultaneous addition of two hydrogen atoms<sup>11)</sup> may lead to the same bimolecular expression. The molecular mechanism is also preferred from the conclusion that the adsorption of hydrogen related with the hydrogenation is weaker than that of either of the olefines, the adsorption heats of which have been found to be about 15 kcal. On some other grounds, a similar mechanism involving molecular hydrogen has been suggested by Twigg.<sup>12)</sup>

#### Summary.

(1) The rate of hydrogenation of propylene has been investigated statically in the temperature range 25—178°C. at pressures of a few cm. Hg, a nickel filament being used as a catalyst.

(2) It has been found that propylene deteriorates the activity of the catalyst in the absence of hydrogen unless the temperature is very low.

(3) The kinetics of the hydrogenation of propylene has much the same characteristics as that of ethylene previously investigated.

(4) The rate of hydrogenation of propylene attains to a maximum value at about 110°C. under the experimental conditions given above.

(5) The reaction curves obtained at high temperatures have been analysed in the same way as in the case of ethylene. It has been thus deduced that the adsorption heat of propylene is about 15 kcal., almost the same value as previously obtained for ethylene, while the activation heat for the hydrogenation of propylene is lower than that for ethylene by about 4 kcal.

(6) Comparisons have been made between the rates of hydrogenation of ethylene and propylene in the temperature range 25—178°C. with the result that propylene is hydrogenated more slowly than ethylene, the difference in the rates increasing with rise of temperature. This suggests that the hydrogenation of propylene has a probability factor much smaller than that for ethylene.

(7) Some experiments carried out with mixtures of ethylene and propylene have shown that the two olefines are hydrogenated with the same relative rates

11) A. Farkas and L. Farkas, *Trans. Farad. Soc.*, **33**, 827, 837 (1937).

12) G. H. Twigg and E. K. Rideal, *Proc. Roy. Soc., A*, **171**, 55 (1939).

as determined from the separate hydrogenation.

(8) Conclusions have been given for the hydrogenation of ethylene and propylene on nickel.

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