THE HYDROGENATION OF ISO-BUTYLENE IN THE PRESENCE OF NICKEL CATALYST.

By Ryô Kiyama.

The kinetics of the hydrogenation of ethylene and propylene has already been studied by O. Toyama[1]. It being desirable to get general information upon the hydrogenation of olefines, in the present experiments, the velocity of the hydrogenation of iso-butylene was measured under various experimental conditions.

Experimental.

The hydrogen used was commercial electrolytic hydrogen in a bomb; it was washed with a pyrogallol-potassium hydroxide solution to remove the oxygen present. Iso-butylene was prepared by dehydrating iso-butyl alcohol with active alumina at 380°C.[2]; the active alumina was prepared by igniting Merck's aluminium nitrate at 450°C. and denitrating with water vapour at the same temperature. The iso-butylene thus obtained was repeatedly distilled; the distilation was checked by measuring the boiling point from the vapour pressure.

The catalyst used for hydrogenation was prepared by igniting Merck's nickel nitrate and reducing it at 450°C.

For the zero instrument the spring pressure gauge made of Telex glass was used. In the reaction chamber holding 50 c.c., 60 milligrams of nickel oxide was placed as catalyst.

(1) Recovery of the Activity of Nickel Catalyst.

The activity of nickel catalyst is generally decreased by olefines, though in the case of ethylene this decrease in activity is not recognizable. In the case of propylene the decay is noticed to a remarkable degree and far more so in the case of butylene. Therefore, to obtain the desired activity of nickel each time there was required the recovery of its activity for every measurement. For this purpose was adopted the method of heating the catalyst with hydrogen after each reaction. In order to determine the best condition for the recovery of the catalyst (90 milligrams of nickel oxide) with hydrogen and iso-butylene in equi-volume, the two different methods, of heating with hydrogen (15 cm.Hg.) and of heating during

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[1] O. Toyama, This Journal, **11**, 353 (1937), **12**, 115 (1938), **14**, 86 (1940).

[2] Ipatiew, Ber., **36**, 1990 (1903).

evacuation, were tried at varying temperatures and durations. The experiment shown in Fig. 1 was carried out with the following result:

Exp. No.	Conditions of Recovery			
	Heating in	Temperature °C	Minute	Recovery
1	hydrogen	300	100	+
2	vacuum	300	100	—
3	hydrogen	200	60	—
4	vacuum	200	90	—
5	vacuum	100	150	—
6	vacuum	100	90	—
7	vacuum	100	30	—
8	hydrogen	300	100	—

The recovery is more satisfactory with hydrogen than by evacuation, and it is dependent on both temperature and time. It was ascertained that 100 minutes' heating at 300°C. with hydrogen is sufficient for the recovery of 90 milligrams or so of nickel oxide used as catalyst.

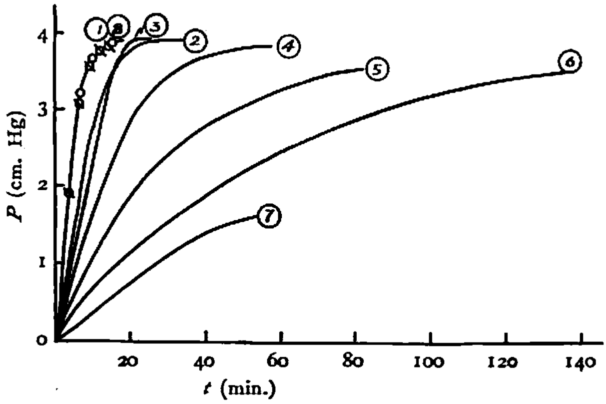

Fig. 1.

(2) Thermal stability of iso-butylene and iso-butylene-hydrogen.

To see whether or not iso-butylene or iso-butylene-hydrogen was affected by heating, the relation between the temperature of heating and pressure was examined. The result is shown in Fig. 2, where (1) and (2) show the thermal expansion of iso-butylene and iso-butylene-hydrogen respectively in the absence of the catalyst. In the case of iso-butylene alone, there is no change below the neighbourhood of 380°C. Such is also the case with iso-butylene-hydrogen even at far higher temperatures. On the other hand, in the presence of nickel catalyst, iso-butylene is unstable and begins to decompose at 300°C. This experiment was followed by

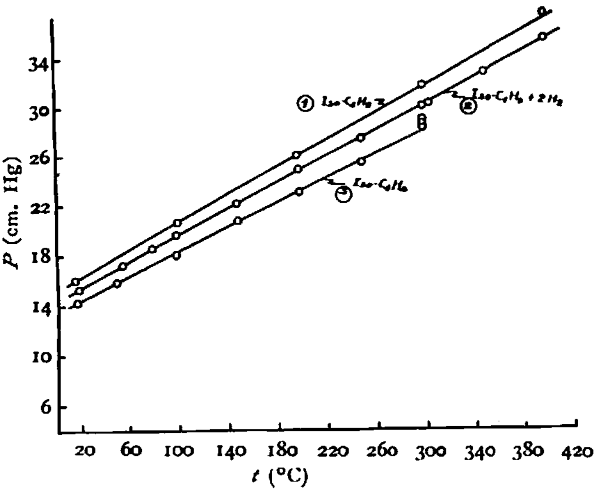

Fig. 2.

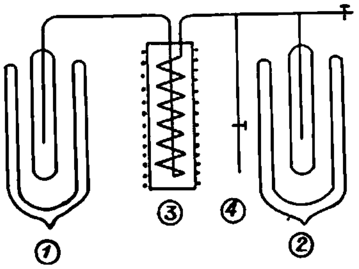

Fig. 3.

another kind of experiment (See Fig. 3.). The traps (1) and (2) containing iso-butylene were immersed alternately in a solid carbon dioxide bath and passed through the heated space (3) repeatedly. The gas was collected by means of a mercury burette from (4) to find its bromine number. The bromine number thus observed was constant within limits of the above relation between pressure and temperature holding linearity. It is inferred, therefore, that no chemical change takes place within the range of the linear relation between pressure and temperature.

(3) The hydrogenation of iso-butylene in the case of iso-butylene-hydrogen in equi-volume.

The decrease in the pressure of the hydrogenation at 70, 90, 110 and 130°C. with the time is expressed in Fig. 4. Let the initial pressure of iso-butylene and

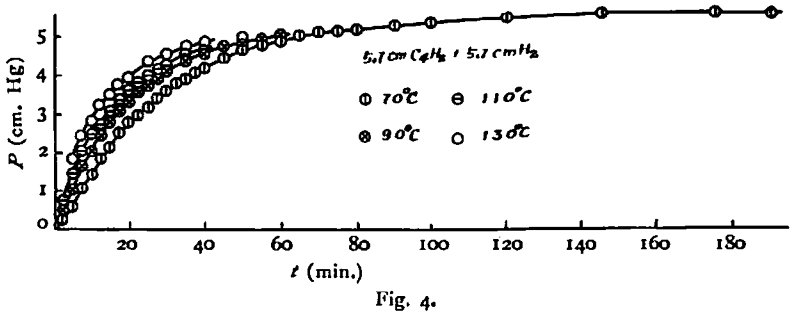

Fig. 4.

the pressure decrease at a time t be represented P_0 and P. respectively, then the velocity of hydrogenation is expressed when it is of the 1st order for iso-butylene, by the following formula;

$$\frac{dP}{dt} = K(P_0 - P)$$

namely,

$$\ln\frac{P_0}{P_0-P}=Kt.$$

Each curve in Fig. 4 gives the relation between $\ln\frac{P_0}{P_0-P}$ and t as shown in Fig. 5. In the $\ln\frac{P_0}{P_0-P}-t$ curve for each temperature, the lower the temperature is, the longer the linear part is. In other words, at the initial stage of the reaction the hydrogenation proceeds as a 1st order type. With rising temperature,

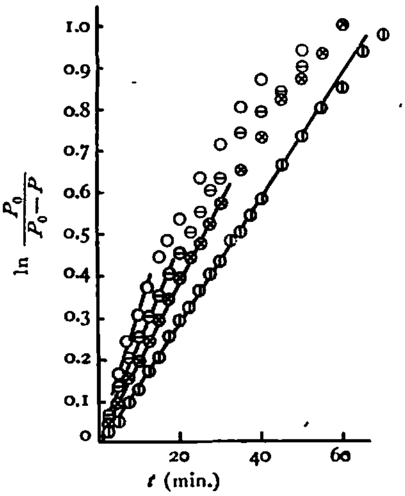

Fig. 5. ⦶, 70°C; ⊗, 90°C; ⊖, 110°C; ○, 130°C.

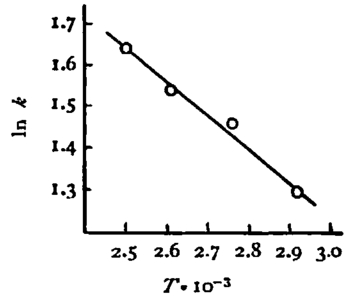

Fig. 6.

its velocity rapidly falls and at the same time poisoning of the catalyst becomes noticeable. The relation between ln K calculated from the initial velocity at each temperature and the absolute temperature reciprocal $\frac{1}{T}$ is linear as shown in Fig. 6. From the slope of this straight line the heat of activation was found to be 1.6 kcals.

(4) The effect of the concentration of hydrogen in the hydrogenation of iso-butylene.

The initial reaction velocities were measured with the gases whose volume ratios, H_2/C_4H_8, were 1, 1.35, 2, and 3 at 70°C. The result is shown in Fig. 7. The increase of hydrogen accelerates the reaction; when the ratio of hydrogen to iso-butylene is above 2, the reaction velocity reaches a maximum, but it falls when the ratio approaches to 3. On the other hand, when iso-butylene is in excess the velocity is smaller than when H_2/C_4H_8 is 1, and the recovery of the catalyst becomes very difficult.

To compare the poisoning of iso-butylene in the case of excess of hydrogen,

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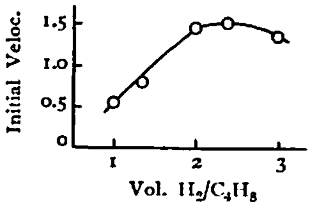

Fig. 7. Temp., 70°C: Iso-C_4H_8, 5.7 cm. Hg.

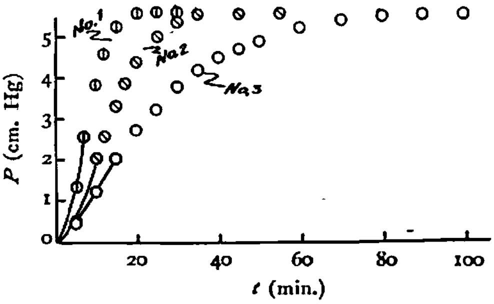

Fig. 8. Temp., 70°C; H_2/Iso-C_4H_8=3; Iso-C_4H_8, 5.7 cm. Hg.

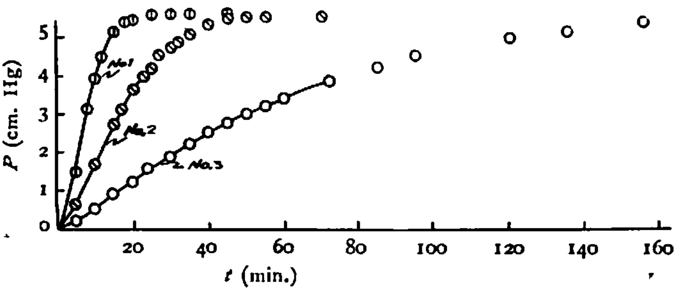

Fig. 9. Temp., 70°C; H_2/Iso-C_4H_8=2; Iso-C_4H_8 5.7 cm. Hg.

reactions were allowed to take place successively in the ratios H_2/C_4H_8 1 : 2 and 1 : 3, using the catalyst evacuated only at the reaction temperature without being recovered. For each ratio, experiments were carried out three times. Figs. 8 and 9 are the cases when $H_2/C_4H_8=3$ and $H_2/C_4H_8=2$ respectively; the numbers on the curves denote the order of the experiments. It is seen that the velocity falls in the order of experiments. The amounts of reaction for 5 and 10 minutes in the two sets of experiments are tabulated for comparison.

H_2/C_4H_8	Amount of Reaction					
	No. 1		No. 2		No. 3	
	t_5	t_{10}	t_5	t_{10}	t_5	t_{10}
2	1.45	3.90	0.60	1.65	0.20	0.50
3	1.35	3.85	0.60	2.05	0.50	1.25

In the presence of the recovered catalyst, reaction No. 1 is a little faster in the ratio of 2 than in the ratio of 3. The reverse is the case in the presence of the catalyst which was not recovered but only evacuated at about the reaction temperature. The $\ln \frac{P_0}{P_0-P}-t$ curves corresponding to Figs. 8 and 9 are given in Figs. 10 and 11 respectively, and neither of them passes through the origin.

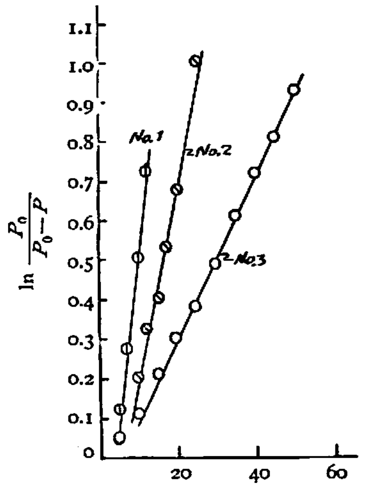

Fig. 10.

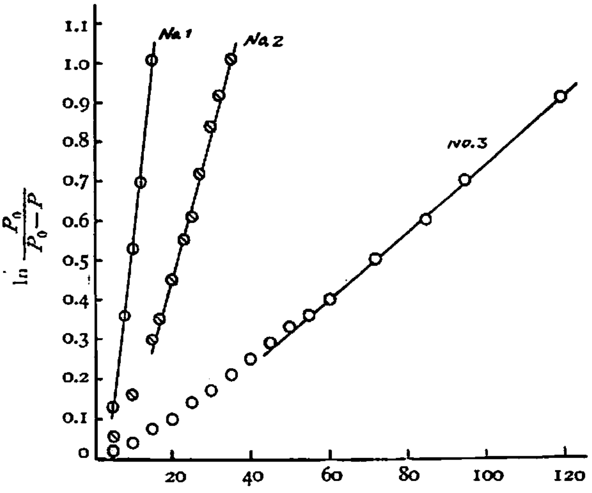

Fig. 11.

Nos. 2 and 3 in Fig. 10 and No. 2 in Fig. 11 break to pass through the origin, while No. 3 in Fig. 11 deflects from the straight line and gradually curves and presents a tendency to pass on the origin. This shows that the velocity which is low at the initial stage of the reaction is gradually accelerated. No. 1 in each figure becomes a straight line because its initial velocity is too high to be measured. The relation between this fact and the degree of the concentration of hydrogen is explained below. Excess of hydrogen prevents the poisoning by iso-butylene from retarding the reaction. This is not so clear in No. 1, whose catalyst is a recovered one, but in Nos. 2 and 3, the process of eliminating the poisoning of iso-butylene is clearly understood. Such an elimination is more intense at higher concentrations. This fact shows that the poisoning in the process of the reaction is affected by hydrogen and it may be connected with the recovery of the catalyst with hydrogen above mentioned.

(5) The effect of oxygen in the hydrogenation of iso-butylene.

To examine the effect of oxygen in the hydrogenation, hydrogen containing 0.2, 0.4 or 0.6% oxygen was used instead of the purified hydrogen mixed with iso-butylene. The reaction process of the respective concentrations of oxygen is given in Fig. 12 under the experimental conditions: $H_2/C_4H_8=\frac{1.26}{1.00}$, the pressure of iso-butylene = 5.0 cm Hg. and 70°C. When a large amount of oxygen is contained, the reaction starts later than with a small amount, but it is gradually accelerated, until it proceeds faster. The relation between $\ln \frac{P_0}{P_0-P}$ and t is shown in Fig. 13. In the case of 0.2% oxygen it maintains a linear relation, but in the

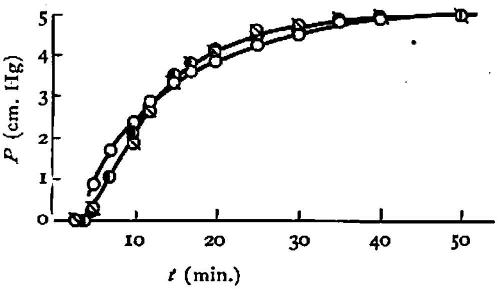

Fig. 12. Temp., 70°C; Iso-C_4H_8, 5.0 Hg cm.; $H_2/C_4H_8=1.26/1.00$. ○, 99.8% H_2+0.2% O_2; ⊘, 99.6% H_2 +0.4% O_2; ◐, 99.4% H_2+0.6% O_2.

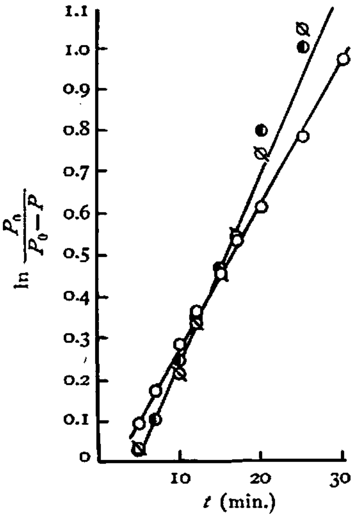

Fig. 13. ○, 99.8% H_2+0.2% O_2; ⊘, 99.6% H_2+0.4% O_2; ◐, 99.4% H_2+0.6% O_2.

case of 0.4 or 0.6% oxygen, though it is so at first, it breaks off the relation in consequence of acceleration. The relation between the change of pressure and time observed in the ratio $H_2/C_4H_8=\frac{1.35}{1.00}$ and at 50°C. is shown in Fig. 14. It takes far more time of retardation for the start of the reaction than in the former case. As seen in Fig. 15, the relation between $\ln\frac{P_0}{P_0-P}$ and t is not linear, the reaction being accelerated. It was found that in the presence of nickel catalyst a trace of oxygen causes a change in the process of the reaction. Oxygen poisons nickel

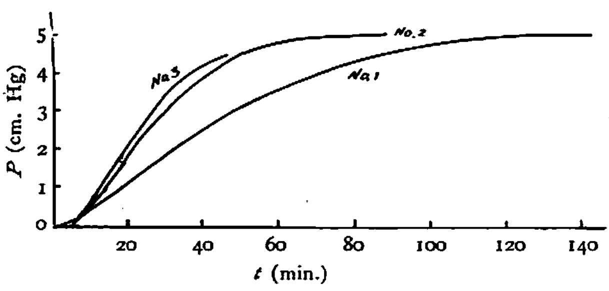

Fig. 14. Temp. 50°C; C_4H_8 5.0 cm. Hg; $H_2/C_4H_8=1.35/1.00$. No. 1, 99.8% H_2+0.2% O_2; No. 2, 99.6% H_2+0.4% O_2; No. 3, 99.4% H_2+0.6% O_2.

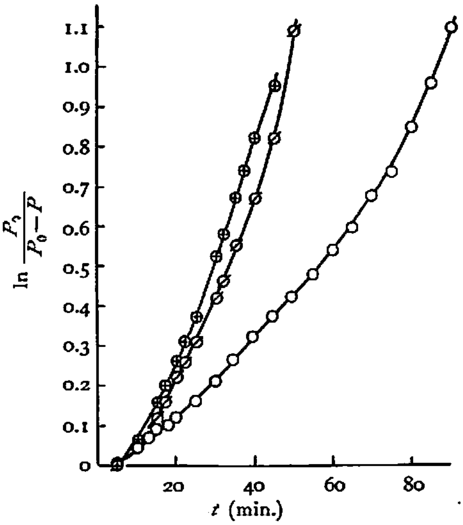

Fig. 15. ○, 99.8% H_2+0.2% O_2; ⊘, 99.6% H_2+0.4% O_2; ⊕, 99.4% H_2+0.6% O_2.

catalyst more intensely than iso-butylene, but it is readily washed away with hydrogen quite unlike iso-butylene, and then it accelerates the reaction by refreshing the surface of the catalyst.

Summary.

1) In the hydrogenation of iso-butylene of several centimeters Hg., the recovery of the activity of the catalyst has been examined.

2) The behaviours of iso-butylene and iso-butylene-hydrogen for thermal conditions and that of iso-butylene in the presence of a catalyst have been statically and dynamically studied.

3) The hydrogenation of an equi-volume mixture of hydrogen and iso-butylene has been observed by a static process at the temperature range of 70° to 130°C. The type of the reaction at the intial stage has been found to be of the 1st order and the activated energy to be 1.6 kcals.

4) The hydrogenation of iso-butylene shows its maximum intial velocity when the amount of hydrogen is above the value twice as large as the stoichiometric value.

5) Using hydrogen of the volume two or three times that of iso-butylene, the hydrogenation velocity has been measured and also the poisoning of iso-butylene examined.

6) In the reaction concerned, a trace of oxygen eliminates the poisoning of iso-butylene and accelerates the reaction.

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