A Kinetic Study of the Hydrogenation of Mesityl Oxide over Unpoisoned and Poisoned Raney Nickel Catalysts. Temperature Variation of the Reaction Order

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The kinetics of the liquid-phase hydrogenation of acetone in *n*-hexane over a Raney nickel catalyst, and of various ketones in cyclohexane over a nickel boride catalyst, have been successfully interpreted by a simplified Langmuir-type rate equation,[1]

$$v = kaC_R/(1+aC_R)^2, \tag{1}$$

where C_R represents the concentration of the reactant to be hydrogenated and where a has the form:

$$a = a_0 \exp(-\delta\Delta G/\boldsymbol{RT}), \tag{2}$$

where $\delta\Delta G$ is the difference between the free energies of the adsorption of the reactant and hydrogen and where a_0 is a constant which is independent of the temperature.

The rate equation has been derived on the following assumptions:

i) Hydrogen and the reactant adsorb reversibly and compete for the same surface sites, whence the ratio of the fractional surface coverage of the reactant(ϑ_R) to that of hydrogen(ϑ_H) is given by[2]:

$$\vartheta_R/\vartheta_H = aC_R \tag{3}$$

The liquid-phase concentration of hydrogen is considered to be independent of the temperature and is included in the a_0 constant.

ii) The surface of the catalyst is fully covered by the adsorbed species of the reactant and hydrogen during the reaction:

$$\vartheta_R + \vartheta_H = 1 \tag{4}$$

iii) The rate-determining step is the surface reaction:

$$v = k\vartheta_R \cdot \vartheta_H \tag{5}$$

where k is the rate constant of the surface reaction.

In this paper the rates of the liquid-phase hydrogenation of the carbon-carbon double bond of mesityl oxide have been measured over a wide range of temperature, and the kinetics of the reaction have been interpreted by Eq. (1).

The rate over the catalyst poisoned by potassium iodide has also been measured, and the kinetics over unpoisoned and poisoned catalysts have been compared. It has been found that the thermodynamic parameter in the rate equation, a, as well as the rate constant decreases as a result of the poisoning.

Experimental

The preparation of the catalyst, the apparatus, and the procedure for the rate measurements were as previously reported.[1]

To poison the catalyst by KI, the sample prepared was added to 10 cc of a KI solution, the concentration of which was 1.07 mol/*l*, and stirred for 10 min. The sample was then washed with water by decantation until no trace of KI was detected. The amount of KI adsorbed on the catalyst by such a treatment was found to be 0.169 mmol/g-Ni.

The analysis by gas chromatography certified that the product of the initial state of the reaction was only isobutyl methyl ketone, the further hydrogenation of which did not proceed until mesityl oxide had been completely hydrogenated. The reaction in this paper is, therefore, concerned with the hydrogenation of the C=C of mesityl oxide.

Results and Discussion

The rate of the hydrogenation of mesityl oxide was found to decrease with an increase in the concentration. The results of the rate measurement

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[1] S. Kishida, S. Kajimoto and S. Teranishi, *Shokubai (Catalyst)*, **9**, 58 (1967); Y. Murakami, S. Kishida, T. Imanaka and S. Teranishi, *ibid.*, **9**, 61 (1967).

[2] G. C. Bond, "Catalysis by Metals," Academic Press, London and New York (1962), p. 124.

at −10°C, −35°C, −50°C, and −78°C are shown in Fig. 1. The peak of the rate expected from Eq. (1) could not be observed, indicating that a is so large that the peak exists in a lower concentration range than the experimental one.

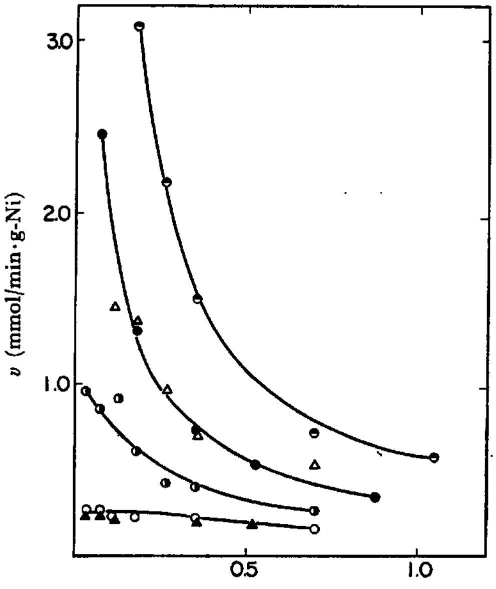

Fig. 1. Hydrogenation of mesityl oxide in n-hexane.
i) on unpoisoned Raney nickel catalyst
◒, −10°C; ●, −35°C; ◑, −50°C;
○, −78°C
ii) on poisoned catalyst
△, −10°C; ▲, −35°C

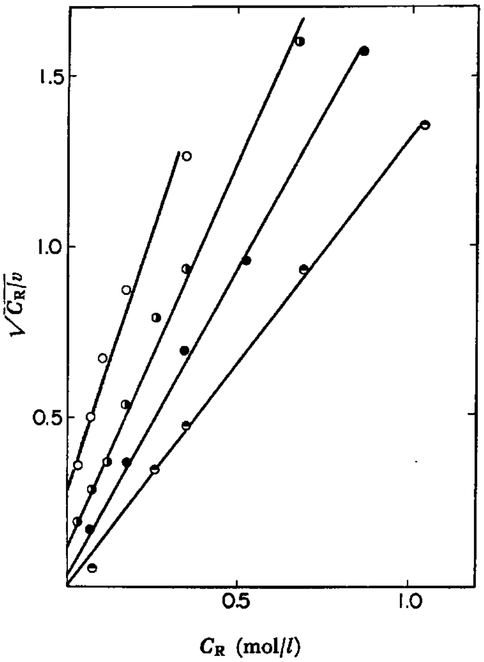

Fig. 2. $\sqrt{C_R/v}$-C_R plots for unpoisoned catalyst.
◒, −10°C; ●, −35°C; ◑, −50°C;
○, −78°C.

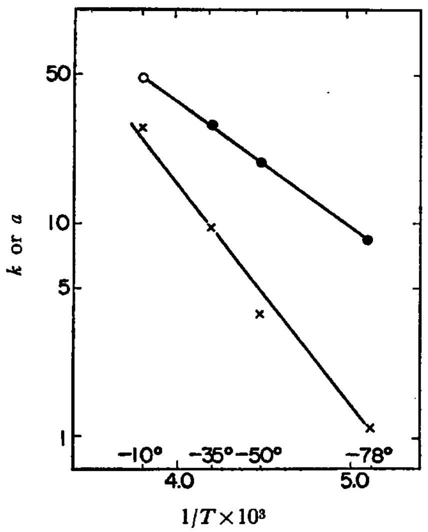

Fig. 3. Arrhenius plot (×) and log a - $1/T$ plot (●) for unpoisoned catalyst.

Since Eq. (1) can be rearranged as:

$$\sqrt{C_R/v} = \sqrt{1/a \cdot k} + \sqrt{a/k} \cdot C_R \qquad (6)$$

the plot of $\sqrt{C_R/v}$ vs. C_R gives a straight line. Figure 2 shows the plots, from which the rate constant and the adsorption parameter, a, can be evaluated at each temperature. However, k and a at −10°C can not be evaluated from the plot, since the plot at −10°C passes through the point of origin. It is obvious from Eq. (6) that the intersect (or the slope) of the plot becomes near zero when a is too large (or too small), and that, in these cases, it is not possible to determine k and a separately. Therefore, a at −10°C was determined by extrapolating the plot of log a vs. $1/T$ (see the open circle in Fig. 3), and k at −10°C was then evaluated from the slope of the plot of $\sqrt{C_R/v}$ vs. C_R.

The rate constants and the adsorption parameters are listed in Table 1. The a increases as the reaction temperature rises, indicating that $\delta\Delta G$ is positive and that the adsorption of hydrogen is stronger than that of mesityl oxide.

The reaction orders with respect to mesityl oxide at each temperature, as evaluated from the plot of log v vs. log C_R, are also listed in Table 1. The order with respect to mesityl oxide becomes lower as the reaction temperature rises.

Since Eq. (1) predicts that the reaction order with respect to the reactant is −1 when $a \cdot C_R \gg 1$ and 1 when $a \cdot C_R \ll 1$, the reaction order determined over the limited concentration range becomes higher as the a value decreases. Therefore, the temperature variation of the reaction order depends

Table 1. Temperature variations of *k*, *a* and reaction order of hydrogenation of mesityl oxide

Temperature (°C)	*k* (mmol/min·g-Ni)	*a* (*l*/mol)	Order of reaction
−78	1.11	8.53	−0.15
−50	3.81	19.7	−0.60
−35	9.60	29.0	−0.75
−10	(27.9)	(48.0)	−1.0
Temperature coefficient (kcal/mol)	4.35	2.63	

on that of *a*. When $\delta\Delta G$ is positive (or negative), the reaction order becomes higher (or lower) with a decrease in the temperature.

It can, therefore, be said that the temperature variation of the reaction order with respect to the A, for example, of a heterogeneous catalytic reaction between A and B, tells us whether the adsorption of A or that of B is stronger.

The rate data measured over the poisoned catalyst at −10°C and −35°C are shown by, respectively, the open and filled triangles in Fig. 1. It was observed that *k* and *a* become smaller by the poisoning. This indicates that the adsorption of mesityl oxide is more inhibited by the poisoning than that of hydrogen.

It has been reported by the present authors that, for the liquid-phase hydrogenation of isobutyl methyl ketone and mesityl oxide over a Raney nickel catalyst,3) the fractional surface coverage of hydrogen in course of the reaction (ϑ_H) is increased by the poisoning. This phenomenon has been interpreted as evidence that the adsorption strength of the reactant is decreased more than that of hydrogen by the poisoning.

Since ϑ_H is given by Eq. (7):

$$\vartheta_\mathrm{H} = 1/(1+a\cdot C_\mathrm{R}) \tag{7}$$

the ϑ_H measured at the same concentration of the reactant increases with a decrease in the *a*.

The poisoning effect on kinetics has scarcely been considered in the literature.4) This phenomenon appears important, however, and has to be taken into account in discussing the mechanism of the poisoning.

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3) S. Kishida, Y. Tanaka and S. Teranishi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **89**, 271 (1968).

4) I. Matsuzaki, T. Nakajima and A. Tada, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **13**, 187 (1966); I. Matsuzaki, A. Tada and T. Nakajima, *Shokubai (Catalyst)*, **8**, 5 (1966).