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Hydrogenation of Various Ketones on Nickel Boride Catalyst

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Kinetic studies on the liquid-phase hydrogenation of various ketones (acetone, methyl ethyl ketone, methyl *n*-propyl ketone and methyl isobuthyl ketone) over nickel boride catalyst were performed. Adsorption measurements of hydrogen in the course of the reactions were also undertaken. The experimental results were successfully interpreted on the basis of the Langmuir-Hinshelwood mechanism with the assumption that the catalyst surface is fully covered with the adsorbed species of hydrogen and ketone during the reaction. The rate constant and the adsorption strength of ketone were found to become larger with increasing number of alkyl carbon atoms.

INTRODUCTION

In the preceding paper (*1*), two of the present authors (S. K. and S. T.) reported kinetic studies on the liquid-phase hydrogenation of acetone over Raney nickel catalyst. Rates were measured in various organic solvents, and the kinetics were interpreted by a rate equation derived on the basis of the Langmuir-Hinshelwood mechanism and on the assumption that the surface of the catalyst is saturated with the adsorbed species of hydrogen, acetone, and solvent during the reaction. It was also suggested that, if the adsorption of solvent can be ignored, the rate equation has a simple form as

$$v = \frac{k a_R C_R}{(1 + a_R C_R)^2}, \quad a_R = \frac{1}{C_H} \exp\left(\frac{-\delta\Delta G_R}{RT}\right) \tag{1}$$

where k and C_R denote, respectively, the rate constant and the liquid-phase concentration of reactant to be hydrogenated, and $\delta\Delta G_R$ is the difference of the free energies of adsorption between reactant and hydrogen. If the mechanism is true, it can be predicted that the surface coverage of hydrogen in the course of the reaction is given by the equation

$$\vartheta_H = \frac{1}{1 + a_R C_R} \tag{2}$$

In this paper the proposed mechanism was examined by testing Eq. (2) directly by measuring the amount of adsorbed hydrogen in course of the reaction. Nickel boride catalyst was found to be preferable for this purpose.

EXPERIMENTAL

Catalyst. Nickel boride catalyst used in the present studies was prepared as described in the literature (*2*), by reducing nickel acetate with sodium borohydride in ethanol-water solution. The procedure was the one designated P-2. The sample was washed, to remove ethanol, water, and acetate ion, five times with isopropyl alcohol and six times with cyclohexane.

Apparatus and procedure. Apparatus and procedure to measure the reaction rate were as described in the previous paper (*1*).

Adsorption measurement of hydrogen during reaction. Figure 1 is a typical run for the adsorption measurement. The amount of catalyst used was 2.35 g Ni. The amounts of cyclohexane and ketone added were weighed by a chemical balance. The volume was kept to be ~40 ml. Before adding ketone, the catalyst was saturated with hydrogen. The amount of hydrogen taken up by the catalyst was designated α_{H0}. (See the first section of Results.) The reacting mixture was sampled by a micro-

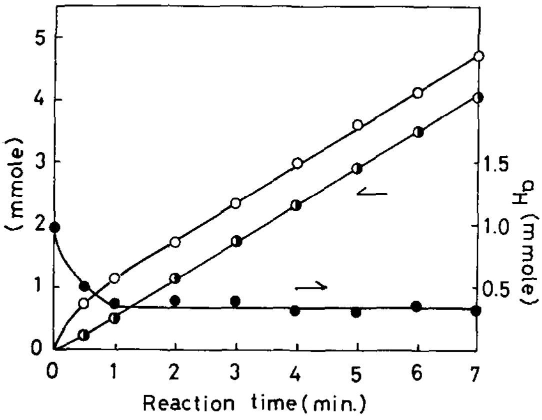

FIG. 1. Determination of the amount of hydrogen adsorbed. Catalyst, 2.35 g Ni; acetone, 9.86 g; cyclohexane, 24.98 g; reaction temperature, 30°C; α_{H0}, 0.99 mmole. ◑, Hydrogen adsorbed; ○, isopropyl alcohol produced; ●, hydrogen adsorbed calculated by Eq. (3).

syringe, and analyzed by gas chromatography to determine the amount of adsorbed hydrogen (α_H) at t minute, which was calculated from a material balance (*3*),

$$\alpha_H = \alpha_{H0} + V_H - W \qquad (3)$$

where V_H is the amount of hydrogen consumed from the gas phase and W the amount of alcohol produced for t minutes. The value of α_H has to be determined at as low a concentration of alcohol as possible, not only because Eq. (3) is valid only when the concentration of alcohol is so low that its adsorption is ignored, but also because the accuracy to which ϑ_H is determined becomes less at higher concentrations of alcohol. Concerning Fig. 1, for example, 2% error in determination of alcohol corresponds to 5% error in ϑ_H at 3 min, and 10% at 6 min. Consequently, in this study, α_H was determined before the amount of alcohol produced reached 5 mmole.

RESULTS

Hydrogen Adsorption

Several experiments were performed on hydrogen adsorption of the catalyst. Results and conclusions may be briefly summarized as follows:

(i) The catalyst washed by cyclohexane was able to take up hydrogen. The amount, designated α_{H0}, was slightly different with various samples, and was 10–12 ml/g Ni.

(ii) Styrene was hydrogenated in nitrogen atmosphere by the catalyst, previously saturated with hydrogen. The amount of ethylbenzene produced was exactly the same amount of hydrogen taken up by the catalyst, indicating that there is no hydrogen originally adsorbed on the surface.

(iii) The catalyst, saturated with hydrogen and then dried in a nitrogen stream at room temperature, was not able to hydrogenate styrene in nitrogen. This indicates that hydrogen taken up by the catalyst is so weakly bound that it easily leaves the surface.

(iv) The BET surface area was 18.5–21.8 m^2/g Ni. The values correspond to 10.2–12.0 ml of hydrogen, if it is assumed that one hydrogen molecule is bound to each Ni atom of the surface (*4*).

From the experimental results briefly summarized in (i)–(iv), it was concluded that the surface of the catalyst is fully covered with ~11 ml/g Ni of the weakly adsorbed hydrogen under 1 atm of hydrogen. Contrary to this, there exist at least two types of adsorbed hydrogen on the surface of Raney nickel catalyst (*5*). The stronger one is not removed even by heating the catalyst. There is some experimental evidence that the weaker one is more reactive. The amount of adsorbed hydrogen during the reaction, determined by a material balance (*3*), includes the two types. It is not possible to measure their amounts individually. This is the reason why nickel boride catalyst is considered to be preferable for the purpose of this study.

Hydrogenation Rate of Ketones

The rate data, obtained for hydrogenation of acetone (A), methyl ethyl ketone (MEK), methyl *n*-propyl ketone (MNPK), and methyl isobutyl ketone (MIBK) in the concentration range of ~1.0–100 wt % at 30°C, are shown in Fig. 2(a), cyclohexane being used as solvent. The rate passes through a maximum, indicating that those reactions proceed by the Langmuir-Hinshelwood mechanism. The peak shifts to higher

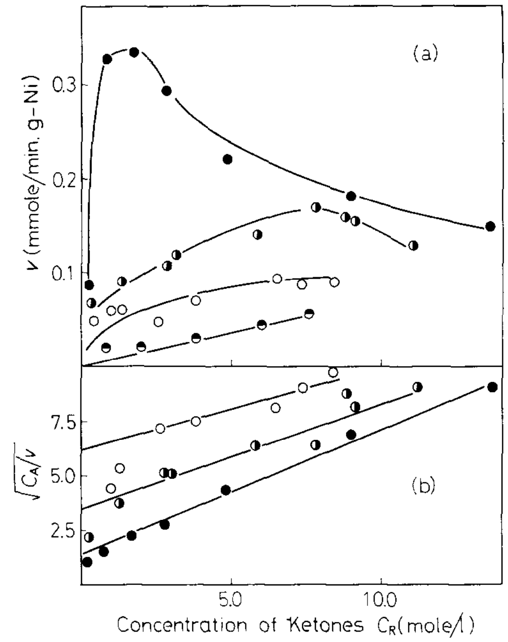

FIG. 2. Hydrogenation of various ketones on nickel boride catalyst in cyclohexane at 30°C; ●, acetone; ◑, methyl ethyl ketone; ○, methyl n-propyl ketone; ◓, methyl isobuthyl ketone. (a) Rate vs. concentration. (b) $(C_A/v)^{1/2}$ vs. C_A.

concentrations, as the reactant varies from A to MEK and MNPK. The reaction of MIBK is of the first order. This indicates that the adsorption of MIBK is very weak, since, if $a_RC_R \ll 1$, Eq. (1) predicts a first order reaction. Therefore, it can be said that a_R, which is a measure of the adsorption strength of ketones, decreases with increasing the number of alkyl carbon atoms, and therefore the peak shifts to higher concentrations* and, for MIBK, it "fades out" from the experimental region of concentration.

Since Eq. (1) can be rewritten as,

$$(C_R/v)^{1/2} = (1/ka_R)^{1/2} + (a_R/k)^{1/2}\,C_R \qquad (4)$$

the plot of $(C_R/v)^{1/2}$ vs. C_R gives a straight line. Rate constants, k, and adsorption parameters, a_R, evaluated from the plot of Eq. 4 [Fig. 2(b)], are listed, respectively, in second and third columns of Table 1. For MIBK, reasonable values were estimated.

Hydrogen Adsorbed during Reaction

The amounts of hydrogen adsorbed during the reaction, α_H, were measured varying ketone concentration. The value, α_{H0}, was measured for every run and the fractional surface coverage of hydrogen, ϑ_H, was calculated by

$$\vartheta_H = \alpha_H/\alpha_{H0} \qquad (5)$$

The results are shown in Fig. 3(a). The coverage of hydrogen decreases with increasing concentration. Interpretation of the results on the basis of the Langmuir-Hinshelwood mechanism is as follows:

If the adsorption of ketone and hydrogen

TABLE 1

THE RATE CONSTANT AND THE ADSORPTION PARAMETER OF VARIOUS KETONES[a]

	k (mmole/min g Ni)	a_R (mole/liter)$^{-1}$	
Acetone	1.23	0.415	0.473
MEK	0.70	0.117	0.115
MNPK	0.38	0.068	0.065
MIBK	0.18	0.056	—

[a] Solvent, cyclohexane; the reaction temperature, 30°C.

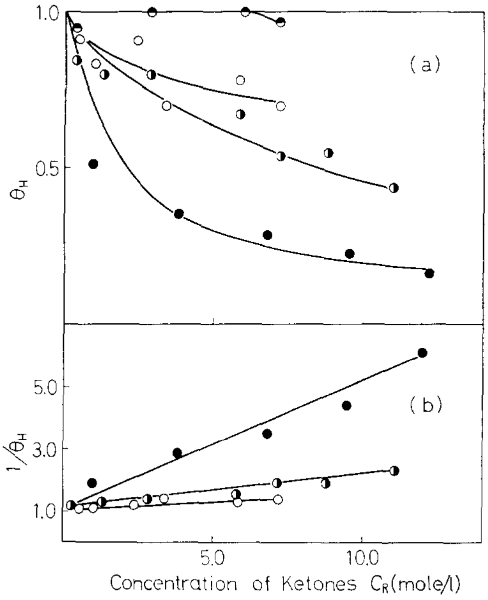

FIG. 3. Adsorption measurement of hydrogen during hydrogenation of various ketones in cyclohexane at 30°C; ●, acetone; ◑, methyl ethyl ketone; ○, methyl n-propyl ketone; ◓, methyl isobuthyl ketone. (a) Concentration dependence of the fractional surface coverage of hydrogen during the reaction. (b) $1/\vartheta_H$ vs. C_A.

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* As pointed out in the preceding paper, the peak appears at $C_R = 1/a_R$.

are in equilibrium during the reaction, the ratio of the fractional surface coverage between ketone (ϑ_R) and hydrogen (ϑ_H) is given by (*1*)

$$\vartheta_R/\vartheta_H = a_R C_R \qquad (6)$$

Introducing the assumption that the surface is fully covered with the adsorbed species of hydrogen and ketone, that is,

$$\vartheta_R + \vartheta_H = 1 \qquad (7)$$

Eq. (2) is derived as was shown in the preceding paper. Since Eq. (2) is rearranged as

$$1/\vartheta_H = 1 + a_R C_R \qquad (8)$$

the plot of $1/\vartheta_H$ vs. C_R gives a straight line, from the slope of which a_R can be determined. The plots are shown in Fig. 3(b) and a_R values, thus evaluated, are listed in column 4 in Table 1. The values are in good agreement with those determined from the kinetic data (column 3). This can be interpreted as the evidence that the whole assumption proposed to interpret the kinetics of the liquid-phase hydrogenation of ketone is true. In Fig. 3(b), slight deviations from the straight line are observed at low concentrations. This may be due to the adsorption of solvent. Anyhow, the quantity of deviations is so small that they can be ignored as experimental errors, indicating that the adsorption of cyclohexane is not large, compared with that of hydrogen and ketone.

The sequence of the adsorption strength of ketones is found to be A > MEK > MNPK > MIBK.

DISCUSSION

According to Ruiter (*6*), the reactivity of open-chain ketones decreases with increasing the total number of alkyl carbon atoms. This is confirmed in this study as is obvious in Table 1. It can immediately be seen from Table 1 that the a_R value as well as the rate constant becomes larger with increasing the number of alkyl carbon atoms. Since a_R is a measure of the adsorption strength of ketone, this would indicate that there exists a correlation between the adsorption strength and the reactivity. Rader and Smith have observed the same phenomenon in the hydrogenation reaction of polymethylbenzene on Adams platinum (*7*) and rhodium catalyst (*8*). They have determined the relative strength of adsorption of polymethylbenzene by means of competitively reducing various binary mixtures of the compounds, and compared it with the relative hydrogenation rate. The strength of adsorption and the reaction rate were found to decrease with increasing the number of methyl groups. They have, however, concluded that the activity is not a direct consequence of the adsorption strength, since they have also observed that, among skeletal isomers, the sequence of the adsorption strength is opposite to that of the activity, for example, the adsorption strength of xylenes is ortho > meta > para, but the reaction rate is the exact reverse (*7, 9*). Moro-oka and Ozaki have reported similar results in the gas-phase oxidation of some olefins over metal oxides (*10*). They have measured the reaction rate and the reaction order in olefin and in oxygen, and compared them with the relative adsorption strength measured by competitively oxidizing various binary mixtures of olefins. It was found that the sequence of the reactivity agrees with that of the adsorption strength, but is the exact reverse of the reaction order in olefin.

The relation between the adsorption strength and the reaction order can be interpreted on the basis of Eq. (1). The equation predicts that, if a_R is so large that it is considered to be $a_R C_R \gg 1$, the reaction order in ketone becomes -1, but 1, if $a_R C_R \ll 1$. In fact, the order is almost -1 in acetone in the wide range of concentration, and 1 in MIBK. It can be said that the reaction orders are between 1 and -1 for MEK and MNPK. Consequently, it would be concluded that the reaction order increases, as the adsorption strength of ketone becomes weaker. This agrees with the conclusion made by Moro-oka and Ozaki from their experiments performed on the gas-phase oxidation.

The reaction order in A, for example, of bimolecular reaction between A and B, could be considered to be an expression of the ratio of the adsorption strength between A and B, if the catalyst surface is fully covered with two reactants during the reaction.

A qualitative correlation between the activity and the adsorption strength, observed by Smith *et al.*, Moro-oka and Ozaki, and now the present authors, appears more interesting, and may be more important. In the present stage of the research, however, the authors can not propose any idea on what the meaning of the phenomenon is.

It should be noted that, in the present study, the a_R value, the thermodynamic parameter in the rate equation, was determined directly by measuring the fractional surface coverage of hydrogen in the course of the ketone hydrogenation.

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