

Kinetics of Liquid-Phase Hydrogenation of Acetone over Raney Nickel Catalyst

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Kinetic studies on the liquid-phase hydrogenation of acetone over Raney nickel catalyst were performed over a wide range of concentration in various solvents. The kinetics in *n*-hexane, cyclohexane, methyl alcohol, and isopropyl alcohol were found to be successfully interpreted on the scheme where hydrogen, acetone, and solvent are adsorbed competitively on the catalyst surface. A rate equation was derived on the basis of the Langmuir-Hinshelwood mechanism. The activation energy was determined to be 10.1 kcal/mole. The relation between the apparent activation energy and the "true" one is also discussed.

INTRODUCTION

It has been well known that in liquid-phase hydrogenation over solid catalysts, the reaction rate depends greatly on the solvent in which the reaction is carried out.

Ruiter and Jungers (1) studied the liquid-phase hydrogenation of various ketones over Ni catalyst. On the relative reactivities of a number of open-chain ketones, they found that the reactivity falls in proportion to the total number of alkyl carbon atoms. On the solvent effect, however, they only mentioned that methanol inhibits the reaction, ethanol is satisfactory, and saturated hydrocarbons are best. Orito and his co-workers (2) have measured the rate of acetone hydrogenation over different Ni catalysts at room temperature in various organic solvents. It was found that saturated hydrocarbons promote the reaction, but primary alcohols and amines inhibit the reaction.

No kinetic model that can explain quantitatively the solvent effect on the reaction rate has ever been proposed for heterogeneous catalysis. In earlier works on such systems, therefore, the conditions where the solvent effect could be ignored were chosen.

Freund and Hulburt (3) studied the hydrogenation of acetone over Raney nickel catalyst using isopropyl alcohol, the product

of the reaction, as the solvent. Kiperman *et al.* (4) have also studied the same reaction using *n*-octane, which they considered to be an inert solvent.

In this laboratory, kinetic studies of the liquid-phase hydrogenation of acetone over Raney nickel catalyst have been made, and the rate data obtained in various organic solvents were found to be successfully interpreted by the rate equation based upon Langmuir-Hinshelwood mechanism, where hydrogen, acetone, and solvent are adsorbed competitively on the catalyst surface.

The apparent activation energy decreases with increasing acetone concentration. It was found that the phenomenon could be interpreted by using the proposed rate equation.

EXPERIMENTAL

Catalyst. Raney alloy (42.0% Ni), 1.2 g was leached with 50 ml of 20% sodium hydroxide solution at 70°C for 30 min. The sample was washed 5 times with 100 ml of water, 5 times with 25 ml of isopropyl alcohol, and 15 times with 25 ml of *n*-hexane under hydrogen.

A fresh sample was used for each experiment. A batch of several samples was prepared at the same time and the test of

reproducibility for every batch was performed with one of the samples by measuring the rate of acetone hydrogenation at 100 wt %. The reproducibility was good.

Apparatus. Apparatus for measuring the reaction rate is shown in Fig. 1. It consisted

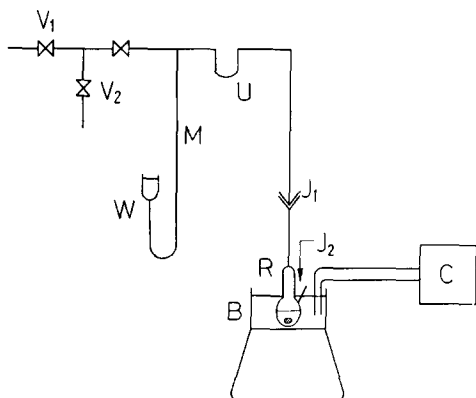


FIG. 1. Apparatus. R, Glass reactor; B, water bath; C, water cooler and circulator; M, manometer; W, water reservoir; U, U-tube with CaCl_2 ; J_1 , glass connector; J_2 , branch; V_1 , V_2 , stopcocks.

of (i) a glass reactor, R; with a magnetic stirrer, contained in a constant temperature bath, B; controlled to $\pm 0.5^\circ\text{C}$ by Coolnix CTR-1A, Komatsu Electronics Inc., C; and (ii) an open-end manometer, M, with a water reservoir, W. The bottom of the reactor was slightly curved so as to keep the stirrer rotating very vigorously. The reactor was connected to the manometer through a U-tube filled with CaCl_2 powder, to seal the reaction system from water vapor. The manifold was connected to a cylinder of hydrogen and a pump, through stopcocks V_1 and V_2 , respectively.

Procedure. Rates were measured by the following procedure. The prepared catalyst was transferred to the glass reactor and dried in a hydrogen stream at room temperature. The specified volume of solvent was admitted from J_2 in the hydrogen stream, and J_2 was sealed with a silicon stopper. The reactor was then connected to J_1 and evacuated and pressured with hydrogen to purge the air. The catalyst was saturated with hydrogen by stirring the catalyst-solvent system for 10 to 30 min (Raney nickel catalyst absorbs 15 ml/g Ni of hydrogen in *n*-hexane).

Acetone was injected from J_2 , the total volume of acetone and solvent being kept to 25 ml. During the course of a given run the water level was continuously adjusted by hand to maintain constant pressure in the apparatus. The volume of hydrogen consumed was measured by following the water level in M. The rapid absorption of hydrogen occurred at the first 30 sec. The rate dropped to be almost constant after 1 min. Therefore, the average volume of hydrogen consumed at the 2nd and 3rd minutes was taken as the reaction rate, v (mmole/min g Ni).

The rate was found to increase and saturate with increasing the stirring. The rate measurement was performed under conditions where the rate is independent of the stirring. The maximum of the apparent activation energy observed in this study is 12 kcal/mole, indicating that the diffusional process plays no role under the conditions adopted.

When necessary, the reaction mixture was sampled from J_2 by a microsyringe and analyzed by gas chromatography. The analysis showed that isopropyl alcohol was the only product of the reaction.

Material. Cyclohexane and *n*-hexane were hydrogenated over Raney nickel catalyst in 1 atm of hydrogen for 2-3 hr, so as to hydrogenate completely the reducible impurities. Other solvents were of reagent grade and used without further purification.

RESULTS AND DISCUSSION

Concentration Dependence of the Rate

By considering the adsorption of hydrogen, acetone, and solvent to be reversible and assuming that these compete for the same surface sites, the ratios of the fractional surface coverages of acetone (ϑ_A) and solvent (ϑ_S) to that of hydrogen (ϑ_H) are given by ($\bar{\nu}$)

$$\vartheta_A/\vartheta_H = (C_A/C_H) \exp(-\delta\Delta G_A/RT) \quad (1)$$

$$\vartheta_S/\vartheta_H = (C_S/C_H) \exp(-\delta\Delta G_S/RT) \quad (2)$$

where $\delta\Delta G_A$ (or $\delta\Delta G_S$) is the difference of the free energies of adsorption between acetone (or solvent) and hydrogen, and C denotes the liquid-phase concentration.

When the reaction rate is measured under a constant pressure of hydrogen, and the difference of the solubility of hydrogen for an acetone-solvent mixture of various compositions is ignored, the liquid-phase concentration of hydrogen, C_H , can be considered to be constant, whence

$$\vartheta_A/\vartheta_H = a_A C_A \quad (1')$$

$$\vartheta_S/\vartheta_H = a_S C_S \quad (2')$$

where $a_A = (1/C_H) \exp(-\delta\Delta G_A/RT)$, and $a_S = (1/C_H) \exp(-\delta\Delta G_S/RT)$. If the rate-determining step is the surface reaction between adsorbed acetone and adsorbed hydrogen, the rate v is proportional to the product of ϑ_A and ϑ_H ,

$$v = k\vartheta_A\vartheta_H \quad (3)$$

where k is the rate constant of the surface

$$v = \frac{ka_A C_A}{\{1 + a_S \rho'_{SA} M'_{AS} C_{A0} + (a_A - a_S \rho'_{SA} M'_{AS}) C_A\}^2} \quad (8)$$

reaction. Since the number of molecules in a unit volume is so large in the liquid phase, compared with that in the gas phase, it can be assumed that the catalyst surface is almost saturated with the three adsorbates in the course of the reaction.

$$\vartheta_A + \vartheta_H + \vartheta_S = 1 \quad (4)$$

This means that the change of the fractional surface coverage of a component, caused by the change of its liquid-phase concentration, necessarily causes the change in those of other components. For example, as ϑ_A decreases, ϑ_S or/and ϑ_H have to increase. The extents of the increases are naturally dependent on the difference of adsorption strength between solvent and hydrogen. In the case where the solvent is adsorbed much more strongly than hydrogen, ϑ_S increases by an amount equal to the decrease in ϑ_A , and therefore ϑ_H can not vary. The opposite phenomenon is expected to occur if the adsorption of hydrogen is much larger than that of solvent. As the reaction rate is determined by the product of ϑ_A and ϑ_H , therefore, the concentration dependence of the rate must be much different according to the adsorption strength of the solvent. This type of solvent effect can be predicted mathematically as follows:

Substituting Eqs. (1') and (2') into Eq. (4)

$$\vartheta_H = 1/(1 + a_A C_A + a_S C_S) \quad (5)$$

and multiplying Eq. (1') by Eq. (5), and substituting the resultant equation and Eq. (5) into Eq. (3), the rate equation of the Langmuir type is obtained

$$v = ka_A C_A / (1 + a_A C_A + a_S C_S)^2 \quad (6)$$

Introducing the relation between C_A and C_S ,

$$M_A C_A / \rho_A + M_S C_S / \rho_S = 1 (= M_A C_{A0} / \rho_A), \quad (7)$$

where M_A and ρ_A are, respectively, the molecular weight and the specific weight of acetone, M_S and ρ_S refer to those of the solvent, and C_{A0} is the concentration of pure acetone (mole/liter), the rate equation is rewritten as a function of acetone concentration

where $\rho'_{SA} = \rho_S / \rho_A$ and $M'_{AS} = M_A / M_S$. For fixed values of k and a_A , the effect of the adsorption strength of the solvent on the reaction rate is calculated from Eq. (8). Figure 2 gives plots of v vs. C_A calculated for selected values of a_S , by fixing both k and a_A to be 1.0. The ratios of the molecular weight (M'_{AS}) and the specific weight (ρ'_{SA}) are also fixed to be 1.0.

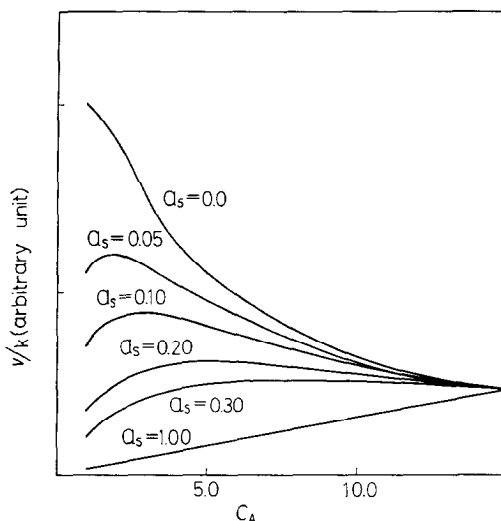


FIG. 2. Plots of v vs. C_A , calculated from Eq. (8); k , a_A , M_S/M_A , and ρ_A/ρ_S are fixed to be 1.0.

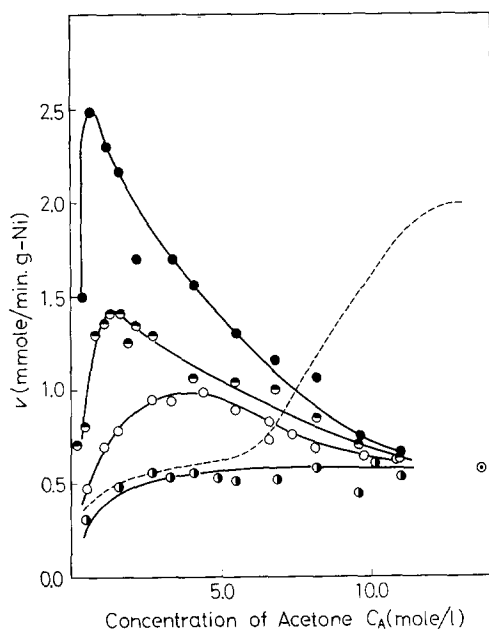


FIG. 3. Acetone hydrogenation of Raney nickel catalyst at 10°C: ●, in *n*-hexane; ●, in cyclohexane; ○, in methyl alcohol; ●, in isopropyl alcohol.

Hydrogenation reactions of acetone over Raney nickel catalyst were performed in *n*-hexane, cyclohexane, methyl alcohol, and isopropyl alcohol at 10°C, varying acetone concentration from ~2 to 100 wt %. The results are shown in Fig. 3. The rate passes through a peak as concentration is increased. This is a typical Langmuir dependence of the rate on concentration. The peak is observed at $C_A = 0.7$ mole/liter in *n*-hexane, and moves to higher concentrations as the solvent varies from *n*-hexane to cyclohexane and methanol, and at the same time the height of the peak becomes lower. In isopropyl alcohol, the peak is hardly observed. The result is in qualitative agreement with the one mathematically predicted, indicating that the effect which those organic solvents have on the reaction are of the type that can be explained by the difference of adsorption strength.

To evaluate a_s , which is a measure of adsorption strength of solvent, Eq. (8) is rearranged,

$$(C_A/v)^{1/2} = (1/ka_A)^{1/2}(1 + a_s\rho'_{SA}M'_{AS}C_{A0}) + (1/ka_A)^{1/2}(a_A - a_s\rho'_{SA}M'_{AS})C_A \quad (9)$$

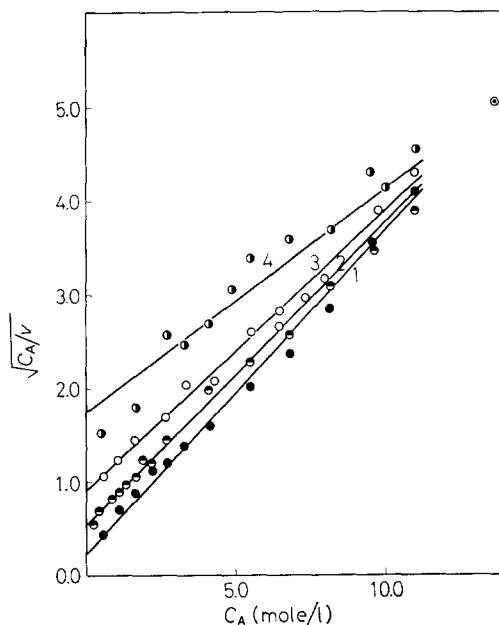


FIG. 4. Plots of $(C_A/v)^{1/2}$ vs. C_A : ●, in *n*-hexane; ●, in cyclohexane; ○, in methyl alcohol; ●, in isopropyl alcohol.

Since the quantities within the parentheses are constant, Eq. (9) predicts a linear variation between $(C_A/v)^{1/2}$ and C_A . The plots are shown in Fig. 4. The usual method, however, is not valid to evaluate a_s , because, in spite of three unknown constants (k , a_A , and a_s) to be evaluated, only two equations can be obtained from the plot of Eq. (9) as,

$$x = (1/ka_A)^{1/2}(a_A - a_s\rho'_{SA}M'_{AS}) \quad (10)$$

$$y = (1/ka_A)^{1/2}(1 + a_s\rho'_{SA}M'_{AS}C_{A0}) \quad (10')$$

where x and y are the values of the slope and the intercept of the plot, respectively.

Since it has been reported in the literature (1, 2) that over Ni catalyst the highest rates have been observed in saturated hydrocarbons for acetone hydrogenation, it is reasonable to assume that a_s of *n*-hexane is zero. In this case, Eq. (8) and Eq. (9) are reduced to Eq. (8') and Eq. (9').

$$v = ka_A C_A / (1 + a_A C_A)^2 \quad (8')$$

$$(C_A/v)^{1/2} = (1/ka_A)^{1/2} + (a_A/k)^{1/2} C_A \quad (9')$$

Those equations are valid for the liquid-phase reaction in a solvent weakly adsorbed. Then, by applying Eq. (9') to the rate data obtained in *n*-hexane (line 1 in Fig. 4), k

TABLE 1
 VALUES OF a_A , a_S , AND RATE CONSTANTS

		Temperature (°C)	
a_A (mole/liter) ⁻¹	—	10°	1.45
	—	0°	1.12
	—	-10°	0.74
	—	-35.5°	0.34
k (mmole/g Ni min)	—	10°	11.0
	—	0°	6.06
	—	-10°	2.40
	—	-35.5°	0.348
a_S (mole/liter) ⁻¹	<i>n</i> -Hexane	10°	(0.00)
	Cyclohexane	10°	0.084
	Methyl alcohol	10°	0.123
	Isopropyl alcohol	10°	0.389

and a_A were evaluated. Thereafter, the a_S of solvent were determined from Eq. (9). The results are listed in Table 1.

It is necessary to point out that the scheme of competitive adsorption does not hold for all cases. For example, as shown in Fig. 3 by a dotted line, the behavior of the reaction rate is much different in water. Similar results are also obtained in some amines (6). These results are not explained by Eq. (8) or Eq. (8'), indicating that k and a_A could change, sometimes due to such solvent effects* such as have been observed in homogeneous systems, other times due to the interaction among the adsorbed species. Therefore, in general, the interaction of solvent with acetone and hydrogen in the liquid phase or in the adsorbed layer has to be taken into account, while the competitive adsorption plays a most important role in the solvents studied here. This problem is now under study in this laboratory. The results will be published in the near future.

Temperature Dependence of Rate

The results of acetone hydrogenation performed in *n*-hexane at 10°, 0°, -10°, and -35.5°C are shown in Fig. 5. Values of k and a_A , determined by Eq. (8') at each tem-

* A referee emphasized the solvent effect of this type, citing literature, for example, H. Hart, F. A. Cassis, and J. J. Bordeaux, *J. Am. Chem. Soc.* **76**, 1639 (1954).

perature, are listed in Table 1. As the reaction temperature decreases, the peak moves to higher concentrations. This fact indicates that the temperature coefficient of a_A is positive, that is, $\delta\Delta G_A > 0$. It can, therefore, be said that hydrogen is adsorbed more strongly than acetone on Raney nickel catalyst. From the plot of $\log a_A$ vs. $1/T$, $\delta\Delta G_A$ was determined to be 4.3 kcal/mole. The

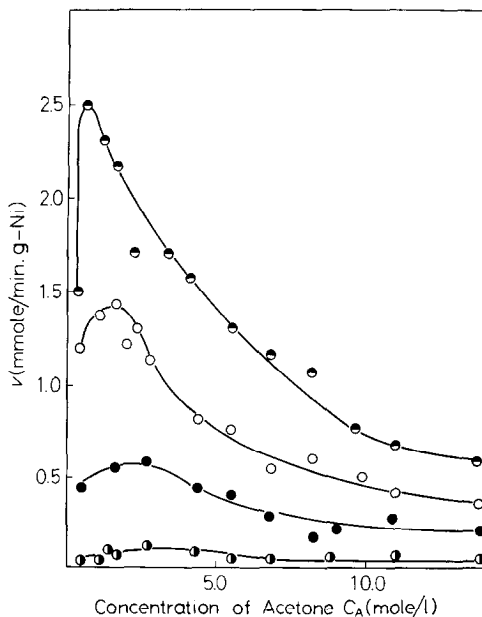


Fig. 5. Acetone hydrogenation on Raney nickel catalyst in *n*-hexane: ●, at 10°C; ○, at 0°C; ●, at -10°C; ●, at -35.5°C.

activation energy was 10.1 kcal/mole. This value is not much different from those obtained by Freund and Hulburt (8.0 kcal/mole) (3), and Jungers *et al.* (≈ 9 kcal/mole) (2), though the rate equations adopted by those authors are different from ours.

In the narrow range of temperature the plot of the logarithm of the rate vs. the reciprocal of absolute temperature gives a straight line. The slope of the plot is usually called an observed or an apparent activation energy (E_v). The relation between the apparent activation energy and the true one (E_k) is easily derived by differentiating Eq. (9') with respect to T and multiplying by RT^2 ,

$$E_v = E_k + \frac{\delta\Delta G_A(1 - a_A C_A)}{(1 + a_A C_A)} \quad (11)$$

Equation (11) indicates that the apparent activation energy depends on acetone concentration.

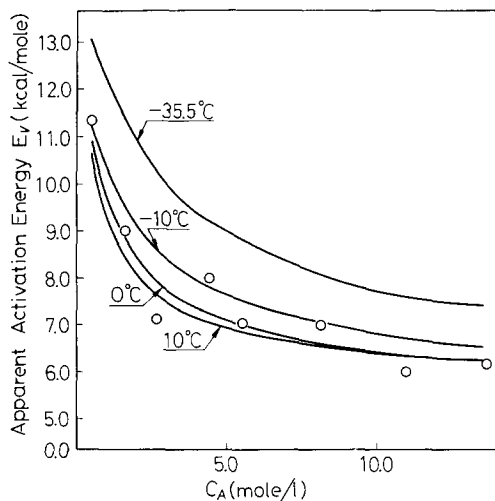


Fig. 6. Concentration dependence of apparent activation energy: O, experimental; real lines, calculated.

At high concentrations ($a_A C_A \gg 1$), the relation is

$$E_v = E_k - \delta\Delta G_A$$

and at low concentrations ($a_A C_A \ll 1$), it is

$$E_v = E_k + \delta\Delta G_A$$

Therefore, if $\delta\Delta G_A > 0$, the apparent ac-

tivation energy is larger at lower concentrations. In fact, E_v is 11.5 kcal/mole at $C_A = 0.5$ mole/liter, and it decreases to 6.2 kcal/mole at 100 wt % ($C_A = 13.78$ mole/liter). The difference must be explained by Eq. (11). In Fig. 6, E_v , determined experimentally in the temperature range of 10° to -10°C , is plotted against concentration C_A . The plots of E_v vs. C_A , mathematically calculated by Eq. (11) at 10° , 0° , -10° , and -35.5°C , are also shown by real lines.

It can immediately be seen from Fig. 6 that the apparent activation energy decreases as temperature increases. This suggests a possibility of interpreting the phenomenon observed sometimes in the liquid-phase hydrogenation of olefinic compounds (6), that the apparent activation energy falls, sometimes to be zero, at higher temperatures. Equation (11) predicts a possibility that if $E_k < \delta\Delta G_R$ (R denotes a reactant to be hydrogenated), the apparent activation energy even becomes negative. Maxted and Moon (7) reported the phenomenon in the liquid-phase hydrogenation of some unsaturated acids over platinum catalyst. This problem is now under study in this laboratory.

The solvent effect on the apparent activation energy can easily be derived from Eq. (6),

$$E_v = E_k + \frac{\delta\Delta G_A}{1 + \frac{2(a_A \delta\Delta G_A C_A + a_S \delta\Delta G_S C_S)}{a_A C_A + a_S C_S}} \quad (12)$$

At low concentrations of acetone ($a_S C_S \gg a_A C_A$, 1), the relation is,

$$E_v = E_k + \delta\Delta G_A - 2\delta\Delta G_S$$

Therefore even at low concentrations, E_v must be small when the adsorption of solvent is strong. This is in qualitative agreement with experimental results reported by Orito *et al.* (2). However, Raney nickel catalyst is an unstable catalyst and the accuracy of the experiment is not enough to make a detailed discussion on this problem possible.

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