Studies on Catalysis by Molten Metal

VI. Kinetics and the Reaction Scheme for the Dehydrogenation of Isopropyl Alcohol over the Liquid Indium Catalyst

YASUO SAITO, FUMIO MIYASHITA, AND YOSHISADA OGINO

*Department of Chemical Engineering, Faculty of Engineering,
Tohoku University, Aramaki Aoba, Sendai, Japan*

The rate of dehydrogenation of isopropyl alcohol over the molten indium (liquid indium) catalyst has been studied in a specially designed reaction apparatus. It has been shown that the rate of reaction is expressed by the following equation:

$$r = k_A K_A^2 p_A^2 / (1 + K_A p_A)^2,$$

where $k_A = 12.7 \exp (-30{,}600/RT)$ in mole cm^{-2} sec^{-1} and $K_A = 6 \times 10^{-2} \exp (9000/RT)$ in atm^{-1}.

In order to explain the kinetic data, reaction schemes have been discussed to indicate that the surface bimolecular collision between the adsorbed alcohol molecules is the rate controlling step. Further, kinetic evidence has been given to consider that the adsorbed alcohol behaves like a two-dimensional gas.

INTRODUCTION

Earlier papers (*1–4*) have shown that many alcohols and amines can be selectively dehydrogenated by certain molten metals. Part of the reaction mechanism (*5*) has been described and the purpose of the present paper is to clarify, as far as possible, the kinetics and mechanism of these reactions. Details of the refined experimental technique and discussion of the results obtained are given here.

EXPERIMENTAL

Apparatus

A schematic representation of the reaction apparatus is given in Fig. 1. As can be seen in this figure, the whole reaction system consists of a vacuum line, a reactant feeding line, and a rate measuring section. The vacuum line serves to evacuate the whole system to $\sim 10^{-3}$ mm Hg pressure. The reactant feeding line is essentially a bulb containing isopropyl alcohol purified by repeated distillations *in vacuo*. This bulb is connected via greaseless cocks to the vacuum line and the rate measuring section which consists of a reactor, a catalyst feeder, and a manometer device.

Procedures

Prior to a series of rate measurements, an appropriate amount of granular metal is charged into the catalyst feeder and evacuated to $\sim 10^{-3}$ mm Hg. During the evacuation, the temperature of the catalyst metal is raised above the melting point of the metal. Then, the molten metal is reduced with purified hydrogen under the following conditions: temperature = 550°C, pressure = 1 atm. After the reduction of 2 hr, the liquid metal is transferred into the reactor by the procedure which is schematically represented in Fig. 2. Namely, the direction of the hydrogen stream is reversed to give a back pressure of hydrogen upon the liquid metal. A careful controlling of this back pressure enables a transfer of an adequate amount of
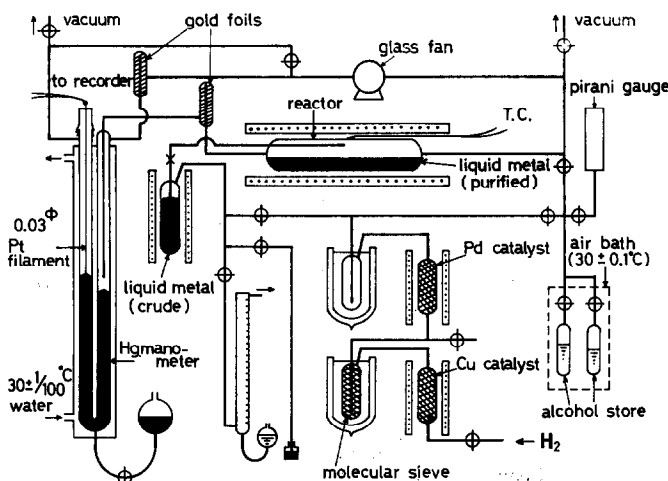
FIG. 1. A schematic representation of the rate measuring apparatus.

the purified liquid metal from the feeder to the reactor, and a contaminated portion of the liquid metal is left in the feeder. During this operation, the temperature of the reactor has to be maintained above the melting point of the catalyst metal. Finally, the pipeline connecting the reactor and the feeder is fused to seal, and the reactor is evacuated again.

After an evacuation of ~4 hr, the temperature of the reactor is adjusted to a desired value; then alcohol vapor is introduced into the reactor, and the circulating fan is driven. The pressure in the reaction system gradually increases as the reaction proceeds. The manometer device serves to the automatic recording of this pressure change.
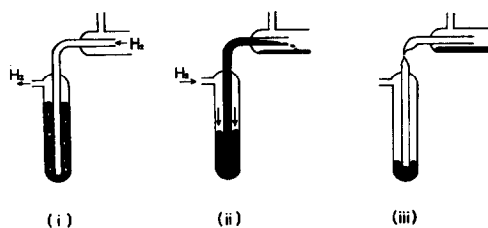

FIG. 2. Procedures of the purification and the transference of the liquid metal catalyst into the reactor: (i) purification by hydrogen streaming, (ii) transference of the liquid metal from the purification tube to the reactor, (iii) final state of the catalyst handling.

The initial rate r_0 of the reaction is evaluated from the slope at the origin of the pressure—time curve appearing on the chart paper. When alcohol vapor is introduced in the reactor, the pressure–time curve exhibits somewhat irregular behavior due to the sudden change in the system pressure. However, the pressure–time curve is easily extrapolated to the origin because the curve becomes essentially straight under a controlled scanning of the recorder chart. Thus, an experiment of a given initial pressure (p_0) yields the corresponding initial rate (r_0). Therefore, a series of experiments of varying initial pressures give a curve representing $p_0 - r_0$ isotherm.

Precautions Against Experimental Error

In order to obtain reliable experimental data, special attention was given to the following points:

(i) An automatic recording of the pressure change was achieved by using a manometer device which is equipped with a bridge circuit. Since a platinum filament (0.03 mm × 1 m) is stretched in the manometer, any change in the mercury level in the manometer causes a resistance change, which is amplified by the bridge circuit and appears on the recorder chart. To ensure a precise and stable recording of the pressure change, the manometer was immersed in a water bath maintained at a

constant temperature of 30° ± 0.01°C and the other part of the bridge circuit laid in an air bath (30° ± 0.1°C).

(ii) Effects of side reactions were proved to be negligible. Preliminary experiments showed that the gaseous products contain more than 98% of hydrogen even at the highest reaction temperature of 554°C. Another gaseous product was methane. Further, acetone was found to be the main condensable product, though traces of acetaldehyde were detected. These data indicate that the effects of the side reaction

$$iso\text{-}C_3H_7OH \rightarrow CH_4 + CH_3CHO$$
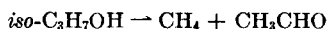
can be neglected.

(iii) Effects of noncatalytic reactions were proved to be negligible. Namely, blank tests without catalyst showed that no significant pressure change occurs even at the highest reaction temperature of 554°C. Therefore, it can be said that the effects of the decomposition of isopropyl alcohol in the bulk phase or on the reactor wall are negligible, especially at the initial stage of the reaction.

RESULTS AND DISCUSSION

Experimental Rate Equations

In an earlier stage of the present work, the equation

$$r_0 = kp_0^{1.2} \tag{1}$$

was found to agree with the experimentally observed $r_0 - p_0$ relations given in Fig. 3. However, it was soon recognized that Eq. (1) is only an empirical equation and hard to be accepted from the viewpoint of the molecular theory of reaction kinetics. Therefore, Eq. (1) was not included in the further discussion in this work.

In order to find the most probable rate equation which is derivable from kinetic treatments based on the molecular theory, rate equations given in Table 1 were compared with the experimental data. The result showed that the two equations

$$r_0 = ap_0^2/(1 + bp_0) \tag{2}$$

and

$$r_0 = ap_0^2/(1 + bp_0)^2 \tag{3}$$

agree well with the experimental data. This is best understood by comparing the linearized forms of the rate equations with the

TABLE 1
RATE EQUATIONS EXAMINED ON THE APPLICABILITY TO THE RATE DATA

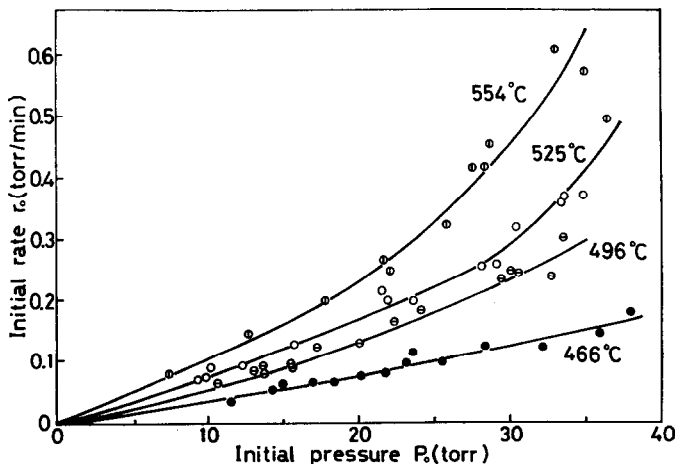|	
1.	$r_0 = ap_0/(1 + bp_0)$
2.	$r_0 = ap_0^2/(1 + bp_0)$
3.	$r_0 = ap_0^2/(1 + bp_0)^2$
4.	$r_0 = ap_0/(1 + bp_0)^2$
5.	$r_0 = ap_0^{1/2}/(1 + bp_0^{1/2})$

FIG. 3. Relations between the initial pressure (p_0) of alcohol vapor and the initial rate (r_0) measured by using the catalyst with a surface area of 17.2 cm².
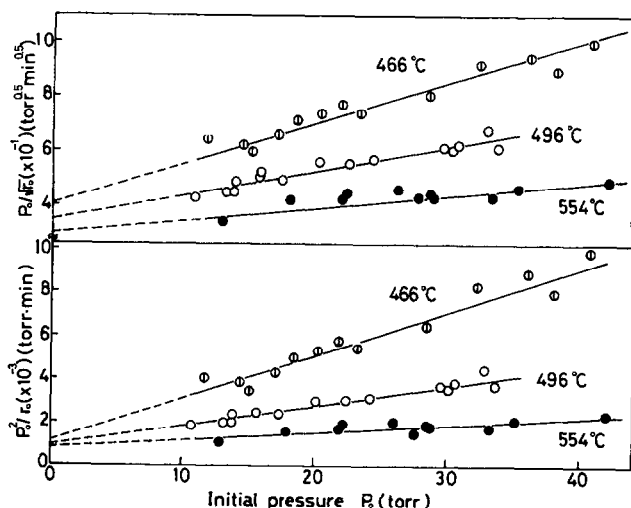
FIG. 4. Respective linear plots of Eq. (4) (lower section) and Eq. (5) (upper section).

experimental data. As can be seen in Fig. 4, both the linearized form of Eq. (2),

$$p_0^2/r_0^* = a^{-1} + a^{-1}bp_0, \qquad (4)$$

and the linearized form of Eq. (3),

$$p_0/r_0^{1/2} = a^{-1/2} + a^{-1/2}bp_0, \qquad (5)$$

were satisfied with the experimental data. Linearized forms of the other rate equations listed in Table 1 were not satisfied with the experimental data.

Theoretical Rate Equations

Theoretical considerations on the rate equations, i.e., Eqs. (2) and (3), enabled us to decide that Eq. (3) is adequate but Eq. (2) is inadequate. Namely, both equations were derived from the corresponding kinetic models and, to examine if they are consistent, the respective rate constants were evaluated and compared with the experimental data. It was shown that Eq. (2) yields an inconsistent result, while Eq. (3) yields a consistent result. The details of the verification are given below.

1. The rate equation (2). The theoretical basis of Eq. (2) is best expressed by the following two assumptions.

(i) The surface reaction takes place between an adsorbed alcohol molecule and a molecule derived by a direct impact from the gas phase.

(ii) The adsorption of alcohol (isopropyl alcohol) obeys a Langmuir-type equation.

These assumptions give the following rate equation:

$$r = k_A K_A p_A^2/(1 + K_A p_A)$$
$$= \Pr Z \exp(-E/RT)K_A p_A/(1 + K_A p_A),$$
$$(6)$$

where k_A is a rate constant, K_A is an adsorption equilibrium constant, Pr is a probability factor, Z is a collision number, and E is an activation energy. A comparison of Eq. (6) with Eq. (2) gives

$$K_A = b \text{ and } k_A = a/b, \qquad (7)$$

provided that $p_0 = p_A$.

According to the kinetic theory of gas (6), the collision number Z is given by

$$Z = p_A/(2\pi m k T)^{1/2}, \qquad (8)$$

where m is the mass of an alcohol molecule, k is the Boltzmann constant, and T is the absolute temperature. Thus, the rate constant becomes

$$k_A = \Pr \exp(-E/RT)/(2\pi m k T)^{1/2}. \quad (9)$$

At a temperature of 798 K, Eq. (9) gives

$$k_A \text{ (calc)} = 7 \times 10^{-3} \Pr \exp(-E/RT), \quad (10)$$

which was compared with the experimental data, i.e.,

$$k_A \text{ [Eq (2)]} = 3 \times 10^{-2} \exp(-E/RT), \quad (11)$$

where both k_A values were expressed in

mole cm^{-2} sec^{-1}. From this comparison, the probability factor was evaluated to be 2.3 × 10. Obviously, this value contradicts the fundamental restriction for the probability factor, i.e., $0 \leq \mathrm{Pr} \leq 1.0$. Therefore, Eq. (2) was thought to be inadequate.

2. The rate equation (3). If we assume that the rate controlling step is a bimolecular collision between the adsorbed molecules (A*) and that the adsorption of alcohol obeys a Langmuir-type equation

$$[A^*] = K_A p_A / (1 + K_A p_A), \qquad (12)$$

then the following rate equation can be derived:

$$r = k_A K_A^2 p_A^2 / (1 + K_A p_A)^2. \qquad (13)$$

The comparison of Eq. (13) with Eq. (3) yields

$$a = k_A K_A^2 \text{ and } b = K_A, \qquad (14)$$

provided that $p_0 = p_A$. The constants k_A and K_A were evaluated from the slopes and the intercepts of the straight lines shown in Fig. 4. The results are shown in Fig. 5. As can be seen in this figure, both k_A and K_A showed normal temperature dependences. They are expressed by

$$k_A = 12.7 \exp(-30,600/RT) \qquad (15)$$

in mole cm^{-2} sec^{-1} and

$$K_A = 6 \times 10^{-2} \exp(9000/RT) \qquad (16)$$

in atm^{-1}.

The values given by Eqs. (15) and (16) seem to be reliable considering from the fairly good coincidence between two kinds of experimental data (○ and ●). Open circles in Fig. 5 indicate data obtained by using the liquid indium catalyst having a surface area of 17.2 cm^2. On the other hand, the black circles indicate data obtained by using the catalyst having a surface area of 40 cm^2. The coincidence between the two kinds of the experimental data shows that the rate of the surface catalysis was successfully measured without significant interference with the thermal decomposition or the diffusion of alcohol vapor.

The theoretical consistency of the rate constant k_A given by Eq. (15) was proved by estimating the value of the two-dimen-
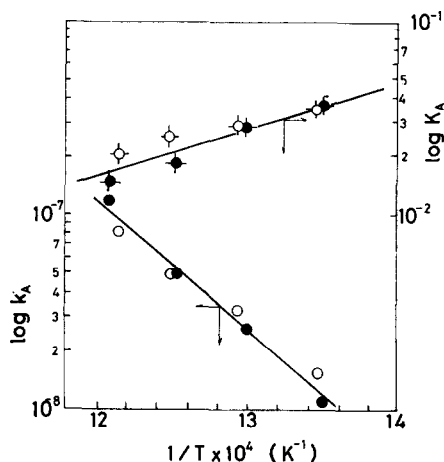

FIG. 5. Temperature dependences of the rate constant (k_A) and the adsorption equilibrium constant (K_A).

sional collision number Z_2, which is formally given by

$$Z_2 = (n/S)^2 (d/4N_0)(4\pi kT/m)^{1/2}, \qquad (17)$$

where n is the number of alcohol molecules adsorbed on the liquid metal, S is the surface area of the liquid metal, d is the diameter of the adsorbed alcohol molecule, and N_0 is the Avogadro number.

On the basis of Eq. (17), the theoretical rate constant $\bar{k}_A$ (calc) (the average in the range of 450–550°C) was evaluated to give,

$$\begin{aligned} \bar{k}_A \text{ (calc)} &= Z_2 \Pr \exp(-E/RT) \\ &= 5 \times 10^2 \Pr \exp(-E/RT) \qquad (18) \end{aligned}$$

in units of mole cm^{-2} sec^{-1}. The comparison of Eq. (18) with Eq. (15) gives the $\mathrm{Pr} = 2.6 \times 10^{-2}$, which is consistent to the relation $0 \leq \mathrm{Pr} \leq 1.0$.

Adsorption Model and Reaction Scheme

The theoretical evaluation of the adsorption equilibrium constant K_A also proved the validity of the surface bimolecular collision mechanism for the catalysis over the liquid indium. If the surface alcohol molecule is assumed to behave as a two-dimensional gas, the theoretical adsorption equilibrium constant K_A (calc) is given by

$$\begin{aligned} K_A \text{ (calc)} &= K_A^0 \text{ (calc)} \exp(q/RT) \\ &= h(kT)^{-1}(2\pi mkT)^{-1/2} \\ &\qquad \times f_{\mathrm{vib}}\sigma \exp(q/RT), \qquad (19) \end{aligned}$$

TABLE 2
Values for the Theoretical $\bar{K}_A{}^0$ and the Experimental $K_A{}^0$

σ, Å^2	$\bar{\nu}$, cm^{-1}	$\bar{f}_{\text{vib}}{}^a$	$\bar{K}_A{}^{0,a}$ atm^{-1} (calc)	$K_A{}^0$, atm^{-1} (obs)
	1	5.4×10^2	1.08×10^{-2}	
25	10	5.3×10	1.06×10^{-3}	
	70	8.2	1.64×10^{-4}	
	1	5.4×10^2	2.18×10^{-2}	
50	10	5.3×10	2.12×10^{-3}	6.0×10^{-2}
	70	8.2	3.28×10^{-4}	
	1	5.4×10^2	4.32×10^{-2}	
100	10	5.3×10	4.24×10^{-3}	
	70	8.2	6.56×10^{-4}	

^{a} Mean values (range 400–600°C).

where f_{vib} is a vibrational partition function, σ is a coarea of the adsorbed molecule, and q is a heat of adsorption. The comparision between $K_A{}^0$ (obs) and $\bar{K}_A{}^0$ (calc) is given in Table 2. As can be seen in this table, the agreement between $K_A{}^0$ (obs) and $\bar{K}_A{}^0$ (calc) is fairly good.

In the evaluation of $\bar{K}_A{}^0$, molecular data were taken from Kemball's paper (7), viz., $\sigma = 20$–30 Å^2 and $\tilde{\nu} - \sim70$ cm^{-1}.[1] Kemball evaluated these values from the adsorption data at temperatures of 25–50°C. Since the reaction temperature of the present work is much higher than the temperature used in the adsorption study of Kemball, exact values of σ and $\tilde{\nu}$ are uncertain. Nevertheless, the agreement between $K_A{}^0$ (obs) and $\bar{K}_A{}^0$ (calc) was found to be fairly good. Further, almost complete coincidence of $K_A{}^0$ (obs) with $\bar{K}_A{}^0$ (calc) can be seen if a lower frequencies of the adsorbed molecule are assumed. This seems to support strongly the consideration that the adsorbed alcohol behaves like a two-dimensional gas. The vibration perpendicular to the surface would not be allowed for an ideal two-dimensional gas.

Previously, Miyamoto and Ogino (5) reported that the adsorbed sec-butyl alcohol behaves like a two-dimensional gas on the surface of liquid metal. The present work

showed that the adsorbed isopropyl alcohol also behaves like a two-dimensional gas. These results provide a basis to consider that the dehydrogenations of sec-butyl alcohol and isopropyl alcohol proceed by a similar mechanism. However, the rate equations for the two reactions are different from each other. Namely, the rate equation for the dehydrogenation of sec-butyl alcohol had been reported (5) to be
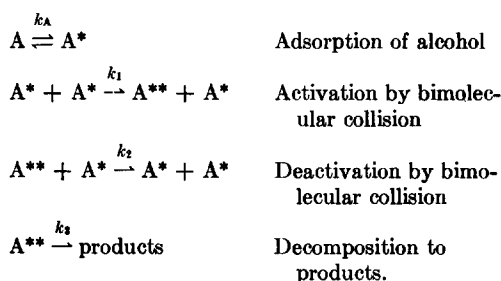
$$r = k'_A p_A / (1 + K_A p_A), \qquad (20)$$

while, according to the present work, the rate equation for the dehydrogenation of isopropyl alcohol was

$$r = k_A K_A{}^2 p_A{}^2 / (1 + K_A p_A)^2. \qquad (13)$$

Therefore, it was suspected that the reaction mechanisms of the two reactions are different.

This suspicion was removed by showing that both Eqs. (13) and (20) are derivable from a common reaction scheme, viz.,

$$A \underset{}{\overset{k_A}{\rightleftharpoons}} A^* \qquad \text{Adsorption of alcohol}$$

$$A^* + A^* \overset{k_1}{\to} A^{**} + A^* \qquad \text{Activation by bimolecular collision}$$

$$A^{**} + A^* \overset{k_2}{\to} A^* + A^* \qquad \text{Deactivation by bimolecular collision}$$

$$A^{**} \overset{k_3}{\to} \text{products} \qquad \text{Decomposition to products.}$$

[1] $\tilde{\nu}$: The frequency of the vibration (perpendicular to the surface) of the adsorbed molecule.

This reaction scheme gives the following rate equation

$$r = k_3[A^{**}] = k_1[A^*]^2/(1 + (k_2/k_3)[A^*]), \quad (21)$$

where

$$[A^*] = \theta = K_A p_A/(1 + K_A p_A). \quad (22)$$

When the adsorption is almost saturated and $(k_2/k_3) [A^*] \gg 1$, Eq. (22) becomes

$$r = k'_A p_A/(1 + K_A p_A), \quad (23)$$

where $k'_A = (k_1 k_3/k_2) K_A$.

This equation is identical with Eq. (20) which had been proved to express the rate of dehydrogenation of *sec*-butyl alcohol. On the other hand, when the surface is sparsely covered and $(k_2/k_3) [A^*] \ll 1$, Eq. (21) becomes

$$r = k_1(K_A p_A)^2/(1 + K_A p_A)^2. \quad (24)$$

This equation is identical with Eq. (13), which was found in the present work.

As mentioned above, the differences in the rate equations for the two alcohols can be considered to arise from the difference in the surface coverage. It had been reported (5) that the dehydrogenation of *sec*-butyl alcohol was carried out under the pressure of $p_A = 0.1$–1 atm. On the other hand, the dehydrogenation of isopropyl alcohol was carried out under the pressure of $p_A = 0.01$–0.1 atm. Therefore, it is plausible to consider that the catalyst surface was almost saturated in the former case, while the surface was sparsely covered in the latter case. Of course, it is also likely that the difference in the surface coverage is due partly to the differences in the physicochemical properties of the two alcohols.

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