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Studies on the Catalysis by the Molten Metal

VIII. Kinetic Isotope Effects Measured by Using a Pulse Reaction Technique

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A pulse reaction technique has been shown to be applicable to study the kinetics of the catalysis over liquid indium. By using this technique, kinetic isotope effects in the catalytic dehydrogenations of ethyl alcohol and isopropyl alcohol over liquid indium have been measured at 460°C to obtain $X_{d_0}/X_{d_1} = 1.62$, $X_{d_1}/X_{d_6} = 1.20$ for ethyl alcohol and $X_{d_0}/X_{d_1} = 1.71$, $X_{d_1}/X_{d_8} = 1.19$ for isopropyl alcohol (X denotes the conversion of alcohol and the subscript d_n indicates a deuterium content in the reactant alcohol). It has been proved that these results are able to be explained in terms of the previously proposed reaction mechanisms. Further, a plausible model of the activated complex has been proposed on the basis of the observed isotope effect.

INTRODUCTION

Previous works (*1–5*) of the present authors have shown that certain liquid metals act as selective catalysts for the dehydrogenations of alcohols and amines. Part of the reaction mechanism has been also clarified (*6,7*) by using specially designed reaction apparatus. However, to confirm the proposed reaction mechanism, further works seem to be required. In this connection, it has been considered that the use of a deuterio compound as a reactant would provide more penetrating information about the mechanism of catalysis over liquid metal. Thus measurements of the kinetic isotope effects for the dehydrogenation of alcohols were made.

In order to save expensive reactant materials, i.e., deuterio alcohols, a pulse reaction technique was used. Although a number of papers which described the use of the pulse reaction technique in studying the heterogeneous catalysis have been published [e.g. (*8,9*)], no application of this technique to the study of catalysis over liquid metal has been reported. Therefore, this paper describes details of the experimental method as well as the theoretical basis of the application of the pulse reaction technique to the kinetic study of catalysis over liquid metal. Further, a discussion is also given of the reaction mechanism by using the observed kinetic isotope effect.

EXPERIMENTAL METHODS

Catalyst and materials. Indium of 99.999% purity was used as a source of the molten metal catalyst. *sec*-Butyl alcohol, ethyl alcohol and isopropyl alcohol of G.R. grade each were used as reactants (we define these alcohols as d_0-alcohols). Deuterio alcohols [ethyl alcohol-d_1 (C_2H_5OD), ethyl alcohol-d_6 (C_2D_5OD), isopropyl alcohol-d_1 (C_3H_7OD) and isopropyl alcohol-d_8 (C_3D_7OD)] were also used (we define these alcohols as d_n-alcohols). The deuterio alcohols were obtained from E. Merck Darmstadt.

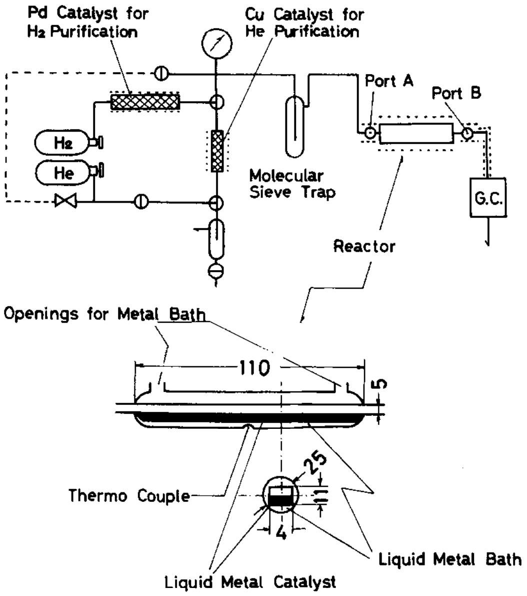


FIG. 1. Flow sheet of the pulse reactor system and the dimensions of the reactor.

Apparatus and procedures. The flow sheet of the experimental apparatus and the schematic representation of the reactor are given in Fig. 1. The reactor is made from Pyrex–glass, and its inner part containing 15 g of liquid metal (In, 99.999%) has a rectangular cross section. The outer part of the reactor has a circular cross section, and it contains an appropriate kind of liquid metal which serves as a heating medium.

Prior to the activity tests and kinetic runs, the catalyst (liquid indium) is reduced by purified hydrogen. The conditions of the catalyst reduction are as follows: temperature = 460 °C, pressure = 2.1 atm, feed rate of hydrogen = 1.3 liters/hr, period = 3 hr.

The activity tests or kinetic runs are carried out in the following manner. Namely, a desired kind of reactant alcohol is injected (0.1–0.6 μl) from the port (A) into the reaction system in which a carrier gas (purified helium) is streaming with a constant flow rate (~ 1 liter/hr). The reaction occurs over the surface of the liquid metal and the products are brought to the gas chromatographic apparatus. The injection port (B) serves the blank test to confirm that the reaction occurs only in the reactor. In the analyses of deuterio compounds a Neva mass filter NAG-520 mass spectrometer is used.

RESULTS

Dehydrogenation of sec-butyl alcohol. The relation between the conversion (X) of *sec*-butyl alcohol and the apparent pulse intensity (N_p) which is defined by the in-

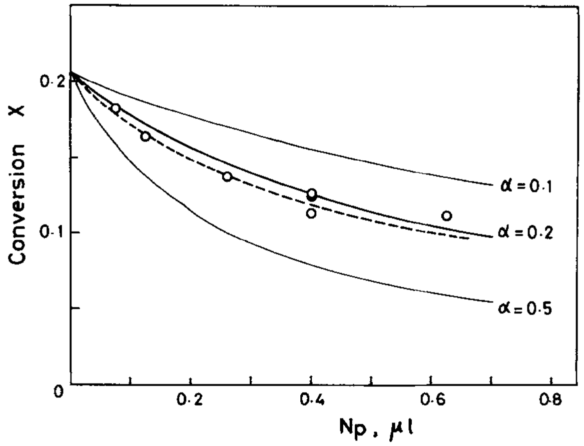


FIG. 2. The relation between conversion (X) of *sec*-butyl alcohol and the apparent pulse intensity (N_p) defined by the injected amount of the alcohol: (O---) experimental values, (—) calculated values.

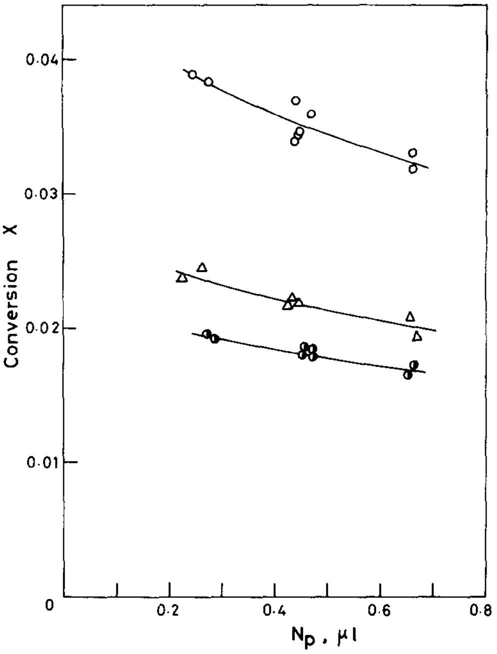


FIG. 3. Relations between the conversions (X) of the d_0-, d_1-, d_6-ethyl alcohols and the apparent pulse intensity (N_p): (O—) C_2H_5OH, (Δ—) C_2H_5OD, (◑—) C_2D_5OD.

jected amount of alcohol is given in Fig. 2. As shown in this figure, the conversion decreased with the increase in the pulse intensity. Further, the gas chromatographic analyses showed that the condensable product is methyl ethyl ketone only. The dehydrogenation of *sec*-butyl alcohol to form methyl ethyl ketone had been reported (*6*) to proceed with a selectivity higher than 95% even at a reaction temperature of 550°C. The present work confirmed the high selectivity of this reaction over the liquid indium catalyst, viz, the selectivity was found to be ~100% at a temperature 460°C. In addition, no appreciable pyrolyzed products were detected in the absence of the liquid indium catalyst. Therefore, the data given in Fig. 2 may afford a quantitative discussion.

Dehydrogenations of ethyl alcohol and isopropyl alcohol. The experimental data for the dehydrogenations of ethyl alcohol and isopropyl alcohol are given in Figs. 3 and 4, respectively. As shown in these figures, the conversion decreased with the increase in the apparent pulse intensity. This tendency is similar to that observed for the reaction of *sec*-butyl alcohol (cf. Fig. 2).

The data for the reactions of the deuterio alcohols are included in Figs. 3 and 4. As shown in these figures, the conversion at a given pulse intensity decreased with the increase in the deuterium content of the reactant alcohol, viz,

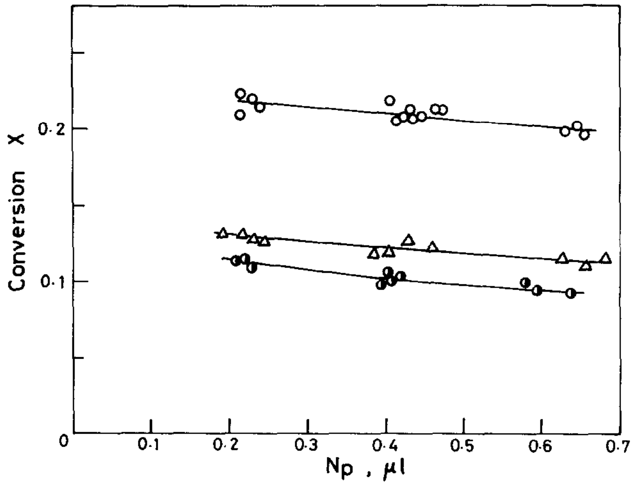


FIG. 4. Relations between the conversions (X) of the d_0-, d_1-, d_8-isopropyl alcohols and the apparent pulse intensity (N_p): (O—) $(CH_3)_2CHOH$, (Δ—) $(CH_3)_2CHOD$, (◑—) $(CD_3)_2CDOD$.

TABLE 1
DEUTERIUM DISTRIBUTION IN THE GASEOUS PRODUCTS

Reactants	Composition of gas: $\frac{HD}{HD + D_2}$	$\frac{D_2}{HD + D_2}$
CH_3CH_2OD	0.96	0.04
$(CH_3)_2CHOD$	0.98	0.02

$X_{d_0} > X_{d_1} > X_{d_{6,8}}$ or more quantitatively,

$$X_{d_0}/X_{d_1} = 1.62, X_{d_1}/X_{d_6} = 1.20,$$

for ethyl alcohol and

$$X_{d_0}/X_{d_1} = 1.71, X_{d_1}/X_{d_8} = 1.19,$$

for isopropyl alcohol. Thus the existence of the kinetic isotope effect became evident.

Results of mass spectrometric analyses for the gaseous products are given in Table 1. As shown in this table, the d_1-alcohols were dehydrogenated to form predominantly HD, and the formation of D_2 were negligible. Further, results of gas chromatographic analyses showed that the dehydrogenations of every d_0-alcohol and every d_n-alcohol proceeded selectively and no appreciable side reactions or thermal decompositions took place.

DISCUSSION

Theoretical Basis for the Pulse Reaction Technique

Many theoretical works on the pulse reactor with a packed catalyst bed have been published and it has been well established that the kinetics of the pulse reactor with a rectangular pulse are identical to the steady state reactor. However, the geometry of the present reactor is different from the packed catalyst bed reactor with a circular cross section. Therefore, prior to the application of the pulse reaction technique upon the kinetic study of catalysis over liquid metal, the theoretical basis of this technique must be clarified. For this purpose, a geometrical model of the reactor is presented in Fig. 5, and the following assumptions were adopted:

i. The carrier gas and the injected reactant vapor form a plug flow and move with a constant velocity u along the z-axis.

ii. The adsorbed amount of the reactant on the catalyst surface is negligibly small compared with the injected amount of the reactant.

The former assumption was made on the basis of a very small variance of the reduced residence time, i.e.:

$$\sigma^2 \simeq 2\frac{ud_t}{192\mathscr{D}} \cdot \frac{d_t}{L} \simeq 10^{-4}.$$

σ^2	variance of the reduced residence time for laminar flow.
d_t	mean diameter perpendicular to flow.
$\mathscr{D}$	alcohol diffusivity.
L	length of catalyst bed.
u	gas velocity.

The same assumption was also adopted in the theoretical study by Hattori and Murakami (*10*). The latter assumption was shown to be valid for the present reactor. Hence the material balance with respect to the A-species within a differential volume

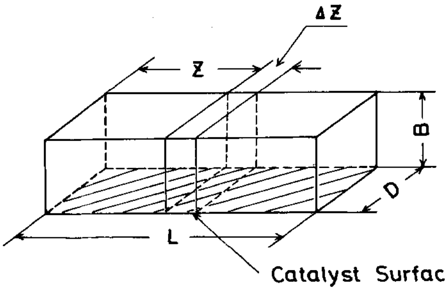


FIG. 5. The geometrical model of the reactor. A: Cross-sectional area of the duct ($A = D \times B$).

element $A\Delta z$ and within a differential time element Δt is given by

$$\underset{\text{(input)}}{AuC_{\mathrm{A}}|_z\,\Delta t} + \underset{\substack{\text{(production}\\ \text{by reaction)}}}{rD\,\Delta z\,\Delta t} = \underset{\text{(output)}}{AuC_{\mathrm{A}}|_{z+\Delta z}\,\Delta t} + \underset{\text{(accumulation)}}{A\,\Delta z\,\Delta C_{\mathrm{A}}}. \qquad (1)$$

If we consider the limits of $\Delta t \rightarrow 0$ and $\Delta z \rightarrow 0$, then Eq. (1) becomes

$$(\partial C_{\mathrm{A}}/\partial t)_z = -u(\partial C_{\mathrm{A}}/\partial z)_t + (D/A)r, \qquad (2)$$

where C_{A} is a concentration of the A-species in the gas phase and r is a rate of production of the A-species per unit of the surface of the catalyst.

If we define a new variable w by

$$w = z - ut, \qquad (3)$$

then Eq. (2) takes a more concise form, viz,

$$(\partial C_{\mathrm{A}}/\partial t)_w = (D/A)r. \qquad (4)$$

In order to facilitate the practical use of the pulse reaction technique, the differential equation [Eq. (4)] was integrated under the assumption that the injected reactant forms a rectangular pulse. The integrated results (X–C^0_{A}), together with the corresponding rate equations, are given in Table 2. Qualitative representations of these relations are given in Fig. 6 (C^0_{A} denotes an inlet concentration of the reactant).

TABLE 2

INTEGRATED FORMS OF SEVERAL RATE EQUATIONS

No.	Rate equation	Formula for the conversion[a] X
1	$r_{\mathrm{A}} = k_1 C_{\mathrm{A}}$	$1 - \exp(-Dk_1 t_m/A)$
2	$r_{\mathrm{A}} = k_2 C^2_{\mathrm{A}}$	$\dfrac{(Dk_2 t_m C^0_{\mathrm{A}}/A)}{1 + (Dk_2 t_m C^0_{\mathrm{A}}/A)}$
3	$r_{\mathrm{A}} = k^0_1 C_{\mathrm{A}}/(1 + K^0_{\mathrm{A}} C_{\mathrm{A}})$	$\dfrac{(Dk^0_1 t_m/A)}{1 + K^0_{\mathrm{A}} C^0_{\mathrm{A}}}\ (X \ll 1)$
4	$r_{\mathrm{A}} = k^0_2 \left(\dfrac{K_{\mathrm{A}} C_{\mathrm{A}}}{1 + K_{\mathrm{A}} C_{\mathrm{A}}}\right)^2$	$\dfrac{(Dk^0_2 K_{\mathrm{A}} t_m/A)}{(1/K_{\mathrm{A}} C^0_{\mathrm{A}}) + 2 + K_{\mathrm{A}} C^0_{\mathrm{A}}}\ (X \ll 1)$

[a] D: width of the reactor: A: cross-sectional area of the duct: C^0_{A}: inlet concentration of the reactant; k_1, k_2, k^0_1, k^0_2: rate constants; K^0_{A}, K_{A}: adsorption equilibrium constants; t_m: contact time.

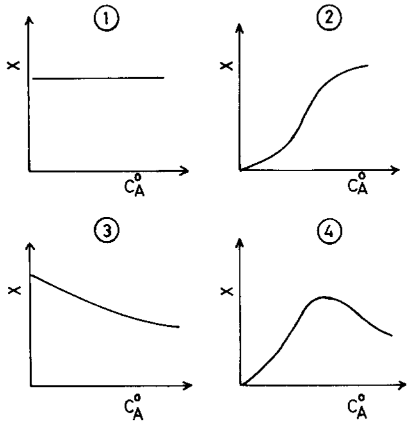


FIG. 6. Schematic representations of the theoretical X–C^0_{A} relations.

Reliability of the Pulse Reaction Technique

The comparison between the theory and experiment was carried out by using the dehydrogenation of *sec*-butyl alcohol as a test reaction. Since the kinetics of this reaction had been fully established (*6*), the comparison of the rate equation determined by the pulse reaction technique with the previously proposed rate equation may provide a basis to examine whether the technique gives a proper rate equation. Further, it had been also reported (*6*) that the selectivity of the dehydrogenation of *sec*-butyl alcohol is exceedingly high. In fact, no appreciable side reactions were observed in the present work. Moreover, no appreciable thermal decompositions took place in the absence of the catalyst. Hence the dehydrogenation of *sec*-butyl alcohol may be regarded as an adequate test reaction.

The experimental X–N_{p} curve given in Fig. 2 has a form similar to that of the theoretical X–C^0_{A} curve (Fig. 6, curve 3). This suggests that the rate of the test reaction may be expressed by

$$-r = r_{\mathrm{A}} = k^0_1\, C_{\mathrm{A}}/(1 + K^0_{\mathrm{A}}\, C_{\mathrm{A}}), \qquad (5)$$

where r_{A} is a rate of disappearance of *sec*-butyl alcohol. On the other hand, the previous work of the present authors (*6*) had shown that a rate equation similar to Eq. (5) was applicable to express the rate of dehydrogenation of *sec*-butyl alcohol. Therefore, it can be said that the pulse reaction technique provides data which are qualitatively consistent with the data obtained by the different experimental method.

A quantitative verification of the validity of the rate equation [Eq. (5)] is also possible. To show this, Eq. (5) has been integrated under the assumption that the inlet vapor pressure p_A^0 of the reactant is proportional to the apparent pulse intensity N_p, viz, $p_A^0 = \alpha N_p$ (α is a proportionality constant). The result is

$$X = (D/A)k_1^0\, t_m/(1 + K_p^0\, p_A^0)$$
$$= (D/A)k_1^0 t_m/(1 + K_p^0 \alpha N_p), \quad (6)$$

where t_m is a contact time defined by L/u. According to the previous work (*6*), the respective values of the rate constant k_1^0 and the adsorption equilibrium constant K_p^0 at 460°C are 0.016 cm/sec and 8 atm^{-1}. Further, the contact time (t_m) of the reactant in the pulse reactor was evaluated to be 6.44 sec. If we use these values, the experimental X–N_p curve is best expressed by a curve theoretically obtained by letting $\alpha = 0.2$ (cf. Fig. 2). A separate experiment showed that $\alpha \approx 0.2$ for *sec*-butyl alcohol and it was found to be independent of temperature.

In the previous work, effects of diffusion on the reaction rate had been proved to be absent (*6*). On the basis of this fact, the previous rate equation had been derived. Therefore, the almost complete coincidence of the rate equation obtained by using the pulse reaction technique, i.e., Eq. (5), with the previous rate equation seems to indicate that the mass transport limitations to the kinetic treatment are negligibly small.

Thus, it has been established that the use of the pulse reaction technique will give reliable information about the kinetics of catalysis over liquid metal.

Kinetic Isotope Effects and the Reaction Mechanism

The present work has revealed that marked kinetic isotope effects appear in the dehydrogenations of alcohols over the liquid indium catalyst. Generally, the kinetic isotope effect is intimately related to the reaction mechanism. Therefore, the observed isotope effects may be explained in terms of the mechanism of the catalytic dehydrogenation of alcohol over the liquid indium. Since part of the reaction mechanism had been already clarified, for the convenience of the discussion, a brief description of it is given below.

1. Previously Proposed Reaction Mechanism

It had been reported (*6,7*) that catalytic dehydrogenation of alcohol over liquid indium proceeds via the following steps, viz,

(a) $A \rightleftharpoons A^*$ (adsorption)

(b) $A^* + A^* \rightharpoonup A^{**} + A^*$ (activation by bimolecular surface collision)

(c) $A^{**} + A^* \rightharpoonup A^* + A^*$ (deactivation by bimolecular surface collision)

(d) $A^{**} \rightharpoonup$ products (decomposition to products by surface unimolecular reaction)

where A, A* and A** denote an alcohol molecule in the gas phase, an adsorbed alcohol molecule and an activated alcohol molecule, respectively. It had been also reported (*6,7*) that the adsorption step is in equilibrium and the adsorbed alcohol behaves like a two-dimensional gas. The rate controlling step had been shown to be the last step (d) unless the partial pressure of the reactant is too small. Thus the adsorption equilibrium constant K_p^0 and the rate constant k_1^0 for the overall reaction had been derived to give

$$K_p^0 = (h/kT)(2\pi mkT)^{-1/2}\,\sigma f_{\text{vib}} \exp(q/RT) \quad (7)$$

and

$$k_1^0 = (kT/h)(2\pi mkT)^{-1/2}\,(hb_a^\ddagger f_{\text{vib}}^\ddagger/b_g) \exp(-E/RT), \quad (8)$$

where the following notations had been employed:

h	Planck's constant
k	Boltzmann's constant
T	absolute temperature
m	mass of an alcohol molecule
σ	co-area of the adsorbed alcohol molecule
q	heat of adsorption
E	activation energy
R	gas constant
f_{vib}	vibrational partition function of the adsorbed alcohol; a vibration perpendicular to the surface had been assumed
$f_{\text{vib}}^\ddagger$	vibrational partition function of the activated complex; a vibration perpendicular to the surface had been assumed
b_g	internal partition function of alcohol in the gas phase
$b_a^\ddagger$	internal partition function of the activated complex.

The right sides of Eqs. (7) and (8) include many factors which may vary with the substitutions of the hydrogen atoms in the alcohol molecule with deuterium atoms. However, the current theory (*11*) of the reaction rate tells that the kinetic isotope effect results mainly from the difference between the zero-point energy of the normal species and that of the deuterio species of the individual compound participating in the reaction and, to a first approximation, contributions from the other factors are negligible. Therefore, according to the theory, only the values of q and E in Eqs. (7) and (8) are considered to vary when the reactant (d_0-alcohol) is replaced by a d_n-alcohol ($n > 0$). Actually, as shown in Table 3, a simple calculation showed that K_p^* which is defined by $(h/kT)(2\pi mkT)^{-1/2}\,\sigma f_{\text{vib}}$ varies little with the above-mentioned deuterium substitution. It may be also possible to prove that k_1^* which is defined by $(kT/h)(2\pi mkT)^{-1/2}(hb_a^\ddagger f_{\text{vib}}^\ddagger/b_g)$ varies little.

2. *Isotope Effect in the Adsorption Stage*

To a first approximation, the heat of adsorption (q_{H}) of the d_0-alcohol and that (q_{D}) of the d_n-alcohol are considered to be equal because the adsorption is weak. According to the previous works (*6,7*), the adsorbed alcohol is considered to behave like a two-dimensional gas and the frequency of the vibration of the adsorbed alcohol is extremely small (~ 70 cm^{-1} or less) (*6,7,12*). These data indicate that the adsorbed molecule is weakly bound by the surface of the liquid metal. Therefore, it is plausible to consider that the adsorption of alcohol will take place without any appreciable changes in the molecular structure. In other words, frequencies of internal vibrations as well as other quantities which characterize the adsorbate alcohol would not vary with the adsorption. Hence the difference between the zero-point energy of the gaseous d_0 alcohol and that of the

TABLE 3

CALCULATED ISOTOPE EFFECTS FOR THE PREEXPONENTIAL FACTORS (K_p^*) OF THE ADSORPTION EQUILIBRIUM CONSTANTS (460°C)

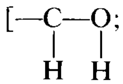
Reactants	K_p^{*b}/K_p^{*a}	K_p^{*c}/K_p^{*b}
Ethyl alcohol	1.000	1.001
Isopropyl alcohol	1.000	1.001

[a] CH_3CH_2OH or $(CH_3)_2CHOH$.
[b] CH_3CH_2OD or $(CH_3)_2CHOD$.
[c] CD_3CD_2OD or $(CD_3)_2CDOD$.

gaseous d_n-alcohol would be conserved even after the adsorption. Consequently, no appreciable difference between q_H and q_D, viz, no appreciable isotope effect would be seen in the adsorption step.

3. Isotope Effect in the Rate Controlling Stage

In order to discuss the isotope effect in the rate controlling stage, a plausible model of the activated complex is necessary. The present authors employed a model which is given in Fig. 7 and, on the basis of this model, the difference in the activation energy $\Delta E_{d_0-d_{1,6,8}} = E_H - E_D$ was evaluated (E_H and E_D denote the activation energies for the d_0-alcohol and for the d_n-alcohol, respectively). Further, the following assumptions were used to facilitate the computation:

i. The frequencies of internal vibrations in the index group  $[\text{—}\underset{\mathrm{H}}{\underset{|}{\mathrm{C}}}\text{—}\underset{\mathrm{H}}{\underset{|}{\mathrm{O}}}$; cf. Ref. (*13*)] do not vary with the change in the carbon number of the reactant alcohol.

ii. The frequency of the C–O stretching vibration is not affected by the substitutions of hydrogen atoms in the index group with deuterium atoms.

iii. In the index group of the activated complex, elongations of the C–H bond and the O–H bond are taking place, and the activated complex is locating at the saddle point of the potential energy surface. Therefore, frequencies of the stretching vibrations of these bonds are very small and negligible.

iv. The frequencies of any desired vibrations can be evaluated by the equation

$$\tilde{\nu} = \nu/c = (2\pi c)^{-1}(k_f/\mu),^{1/2} \tag{9}$$

where c is the velocity of light, k_f is a force constant and μ is a reduced mass.

v. The frequency of the C–H stretching vibration is 2900 cm^{-1} and that of the O–H stretching vibration is 3650 cm^{-1}(*14*).

The proposed model for the activated complex as well as the above-mentioned assumptions give the following expression, viz,

$$\Delta E_{d_0-d_1} = (ch/2)\ [(\tilde{\nu}_{H\cdots H} - \tilde{\nu}_{H\cdots D}) - (\tilde{\nu}_{O-H} - \tilde{\nu}_{O-D})]. \tag{10}$$

Similarly, the expressions of the energy differences for the other d_n-alcohols can be derived. Thus it was possible to evaluate the degree of the kinetic isotope effect as a function of the frequency of stretching vibration between the two hydrogen atoms in the index group of the activated complex, and the calculated results are summarized in Fig. 8. If we assume that $\tilde{\nu}_{H\cdots H} = 3600$ cm^{-1} then this figure gives

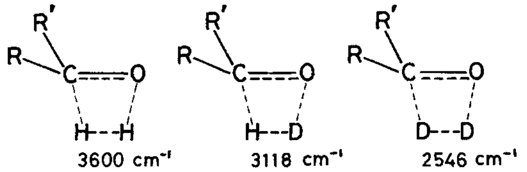


FIG. 7. Models for the activated complexes.

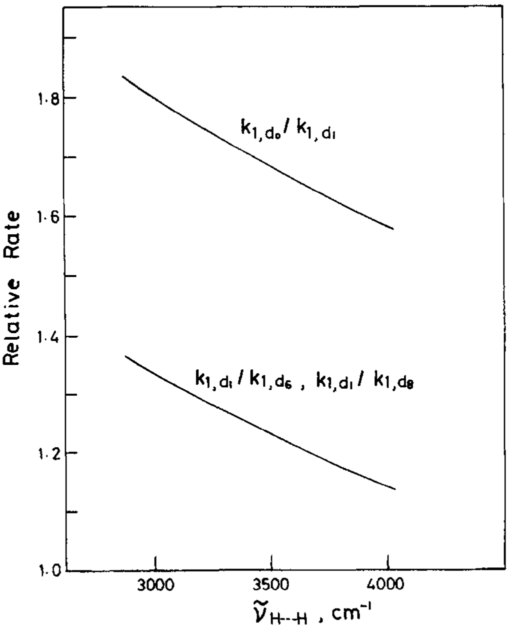


FIG. 8. Calculated values of the kinetic isotope effect in the dehydrogenation of alcohols.

the following relations, viz,

$X_{d_0}/X_{d_1} = k_{1,d_0}/k_{1,d_1} = 1.66$
(both ethyl alcohol and isopropyl alcohol)
$X_{d_1}/X_{d_6} = k_{1,d_1}/k_{1,d_6} = 1.22$
(ethyl alcohol)
$X_{d_1}/X_{d_8} = k_{1,d_1}/k_{1,d_8} = 1.22$
(isopropyl alcohol)

These results agree fairly well with the experimental results, viz,

$$X_{d_0}/X_{d_1} = 1.62 - 1.71 \text{ and } X_{d_1}/X_{d_{6,8}} = 1.19 - 1.20.$$

The assumed frequency, i.e., $\tilde{\nu}_{\mathrm{H---H}} = 3600\ \mathrm{cm}^{-1}$, is smaller than the frequency of the H—H stretching vibration ($\tilde{\nu}_{\mathrm{H-H}} = 4395\ \mathrm{cm}^{-1}$, 15) in molecular hydrogen. This is probable because the bond length between two hydrogen atoms in the index group should be larger in the activated complex than in the reaction product, i.e., hydrogen. Further, the proposed model for the activated complex of the d_1-alcohol should yield gaseous products containing only HD. This is consistent with the experimental result shown in Table 1.

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