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Studies on the Catalysis by the Molten Metal

IX. A Comparison between the Isotope Effect of Two-Dimensional Dehydrogenation and the Isotope Effect of Three-Dimensional Dehydrogenation of Methyl Alcohol

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A semiempirical SCF-MO (MINDO/2) method has been applied to evaluate energy changes of a hypothetical unimolecular dehydrogenation of methyl alcohol in the three-dimensional gas phase. The calculated results have been used to make a potential energy surface and to determine the atomic configuration of the activated complex. It has been shown that the kinetic isotope effect calculated by using the proposed activated complex model agrees well with the observed isotope effect for the dehydrogenation of methyl alcohol over the liquid indium. The implication of this agreement has been discussed from two different standpoints.

INTRODUCTION

Earlier works (*1–6*) of this series have shown that certain liquid metals which have smaller work function act as selective catalysts for the dehydrogenations of alcohols and amines. Rate equations and reaction schemes have been also given to the catalyses by carrying out kinetic experiments (*7, 8*). Further, a model of the activated complex has been proposed by analyzing kinetic isotope effects (*9*).

Since the surface catalysis over the liquid metal has been proved to proceed via a two-dimensional unimolecular reaction mechanism (*7, 8*), it is interesting to compare the experimental results on the catalysis of liquid metal with an appropriate three-dimensional unimolecular reaction. Thus, a semiempirical SCF-MO(MINDO/2) method was applied to the dehydrogenation of methyl alcohol in the gas phase and the kinetic isotope effect was calculated to compare the calculated result with the experimentally observed one for the dehydrogenation of methyl alcohol over the liquid indium.

METHODS

EXPERIMENTAL ISOTOPE EFFECT FOR METHANOL DEHYDROGENATION OVER THE LIQUID INDIUM

The kinetic isotope effect for the dehydrogenation of methyl alcohol over the liquid indium catalyst was measured by using the pulse reaction technique reported in the preceding paper (*9*), and the results are given in Table 1 which includes data for the other alcohols [(*9*) ethyl alcohol and isopropyl alcohol]. As shown in Table 1, the values of the isotope effects for methyl alcohol are nearly equal to the previously obtained values for the other alcohols. This result supports the theory that the mecha-

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TABLE 1

EXPERIMENTAL RESULTS OF THE KINETIC ISOTOPE EFFECTS FOR THE DEHYDROGENATION OF ALCOHOLS OVER LIQUID INDIUM CATALYST[a]

Alcohols	X_{d_0}/X_{d_1}	$X_{d_1}/X_{d_{4,6,8}}$	Reaction temp (°C)
Methyl alcohol	1.74	1.37	475
Ethyl alcohol[b]	1.62	1.20	460
Isopropyl alcohol[b]	1.71	1.19	460

[a] X: conversion; d_0: CH_3OH, CH_3CH_2OH, or $(CH_3)_2CHOH$; d_1: CH_3OD, CH_3CH_2OD, or $(CH_3)_2CHOD$; d_4: CD_3OD; d_6: CD_3CD_2OD; d_8: $(CD_3)_2CDOD$.

[b] Cited from Ref. (9).

nism of the dehydrogenation of methyl alcohol would be the same as those of the other alcohols. In other words, the dehydrogenation of methyl alcohol over the liquid indium can be considered to proceed via a two-dimensional unimolecular mechanism which had been proved to be applicable to the dehydrogenations of the other alcohols over the liquid indium.

RESULTS AND DISCUSSION

THEORETICAL ISOTOPE EFFECT FOR METHANOL DEHYDROGENATION IN THREE-DIMENSIONAL GASEOUS PHASE

Reaction Model and Method of Computation

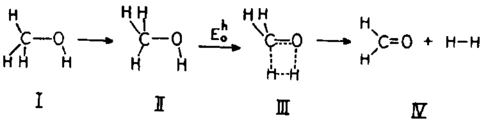

FIG. 1. The reaction model for the dehydrogenation of methyl alcohol: I: energetically most stable methyl alcohol in the gas phase (initial state); II: pseudo-initial state in the gas phase; III: activated state in the gas phase; IV: final state of the reaction in the gas phase.

The reaction model for the methanol dehydrogenation in the three-dimensional gaseous phase is given in Fig. 1. A unimolecular reaction pathway I → II → III (activated complex) → IV was assumed and it was attempted to draw a potential energy surface for this reaction. In order to make energy calculations for the hypothetical methyl alcohol molecules with varying atomic configurations, variables representing the molecular structure are defined in Fig. 2 and a semiempirical SCF-MO (MINDO/2) method (*10, 11*) was applied. Parameters necessary for the calculation were taken from the report of Bodor *et al.* (*11*), and the calculated results were corrected by the same way as that of Bodor *et al.* Further, the following simplifications were made to facilitate the calculation; $\theta_3 = \theta_4$, $r_1 = 1.09$ Å, and $r_3 - r_5 = 0.13$ Å. Further, an auxiliary parameter t was introduced to combine the variables r_2, θ_1, and θ_2 in the following manner:

$$r_2 = 1.43 - (1.43 - 1.21)t \text{ (Å)},$$
$$\theta_1 = 55.90(1 - t) \text{ (deg)},$$
$$\theta_2 = 109.45 + (120.0 - 109.45)t \text{ (deg)}.$$

Of course, these simplifications give a proper atomic configuration of the initial state II ($\theta_3 = 109.45°$, $\theta_4 = 110°$, $r_3 = 1.09$ Å, $r_4 = 0.96$ Å, $r_3 - r_4 = 0.13$ Å, and $r_1 = 1.09$ Å). To assure the reliability of the calculated results, recalculations without such simplifications as above were also

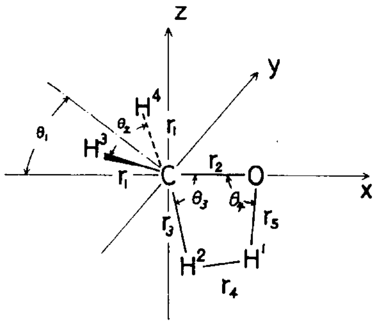

FIG. 2. Atomic configuration model for the methyl alcohol molecule: r_1: C–H^3 or C–H^4 bond length; r_2: C–O bond length; r_3: C–H^2 bond length; r_4: H^1–H^2 bond length; r_5: O–H^1 bond length; θ_1: the angle between the x-axis and the bisector of $\angle H^3CH^4$; θ_2: $\angle H^3CH^4$; θ_3: $\angle H^2CO$; θ_4: $\angle H^1OC$.

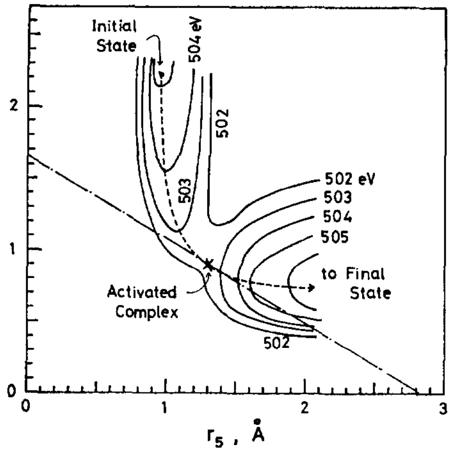

FIG. 3. Potential energy surface for the gas phase reaction $CH_3OH \rightarrow HCHO + H_2$.

carried out in the vicinity of the saddle point (activated state) on the potential energy surface which had been determined by a preliminary calculation. All numerical computations were carried out with a NEAC 2200-Model 700 digital computer (Computer Center, Tohoku University).

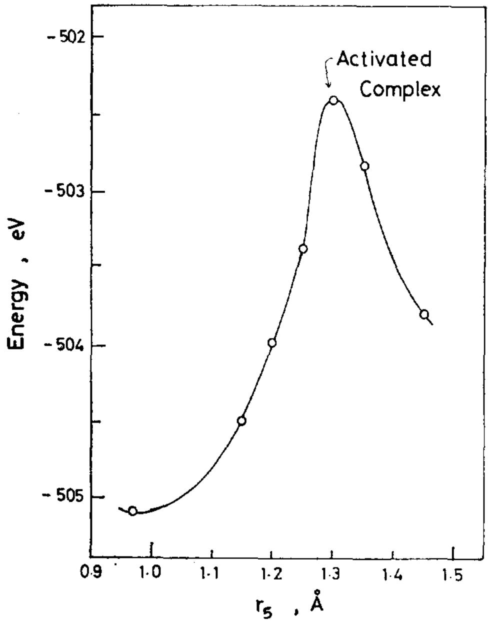

FIG. 4. The relation between the potential energy and r_5(O–H^1 bond length).

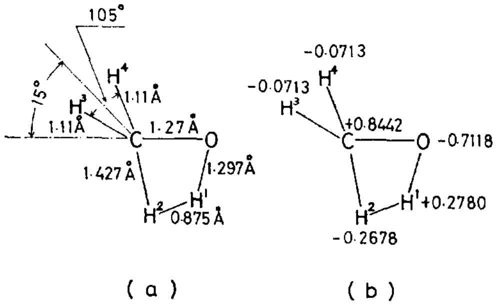

FIG. 5. The configuration (a) and the charge distribution (b) of the activated complex.

Potential Energy Surface, Configuration of Activated Complex

The calculated potential energy surface is given in Fig. 3. This figure represents the potential energy as a function of r_4 (H^1–H^2 bond length) and r_5 (O–H^1 bond length). In this figure, r_2 (C–O bond length) is taken so as to give the minimum energy at any point on the $r_4 \times r_5$ plane. From Fig. 3 we get Fig. 4, wherein the relation between the potential energy and r_5 is given (r_4 is taken so as to give the minimum energy at a given r_5 value). Figures 3 and 4 reveal the manner of the variation of the atomic configuration during the activation of a methyl alcohol molecule. For instance, O–H^1 bond length increases on activation from 0.96 Å (initial state) to 1.297 Å (activated state). In this manner, the atomic configuration of the activated complex can be obtained to give Fig. 5.

Activation Energy

The activation energy $E_0{}^h$ was evaluated to be 61.8 kcal/mol from the difference between the potential energy of the activated state III and that of the initial state I [the state II can be regarded as the initial state because the energy difference between I and II is very small (~0.5 kcal/mol)]. The calculated value of the activation energy is nearly equal to the value of 68 kcal/mol which has been reported by Fletcher (*12*) for the thermal dehydrogenation of methyl alcohol in the gaseous phase ($CH_3OH \rightarrow H_2 + HCHO$; 627–730°C). The discrepancy between the E_0^h (61.8 kcal/mol) and Fletcher's value may be attributed partly to the experimental error of Fletcher's work in which uncertainties due to the wall reactions are appreciable and partly to the simplified model of the present theory. In any case, considering from the general accuracy (±2.8 kcal/mol) of the energy calculation based on the MO-treatment, the coincidence between the theoretical activation energy and the experimental activation energy is fairly good. Therefore, at least to a first approximation, the model proposed in this work is considered to be available to simulate the thermal dehydrogenation of methyl alcohol.

Kinetic Isotope Effects

The potential energy surface given in Fig. 3 as well as the activated complex model given in Fig. 5 can be used to estimate theoretical isotope effects. According to Fig. 5, the bond length of C--H^2 and O--H^1 are considerably elongated compared with their normal values. On the contrary, the separation between H^1--H^2 is comparable with the H-H bond length of normal hydrogen. Therefore, it is an easy work to evaluate the kinetic isotope effect if the directions of the in-phase stretching vibrations of both O--H^1 and C--H^2 are parallel to the reaction coordinate. Unfortunately, however, that is not the case. As shown in Fig. 3, every vibrations of O--H^1, C--H^2 and H^1--H^2 at the saddle point are not parallel (or orthogonal) to the reaction coordinate.

One possible way to overcome this difficulty is to consider the isotope effects for the following two limiting cases, and then hybridize the results. One limit is the case where the O--H^1 mode and the C--H^2 mode are parallel to the reaction coordinate and H^1--H^2 mode is orthogonal to the reaction coordinate, and the other limit is the case where H^1--H^2 mode is parallel to the reaction coordinate and both modes of the O--H^1 and the C--H^2 are orthogonal to the reaction coordinate.

Case 1. In the limiting case where the O--H^1 mode and the C--H^2 mode are parallel to the reaction coordinate and the H^1--H^2 mode is orthogonal, changes in the H^1--H^2 vibration energy would predominantly contribute to the changes in the zero-point energy of the activated complex (*9*), when the hydrogen atoms H^1 and H^2 are partially or totally substituted by deuterium atoms. Thus, the theoretical isotope effects can be evaluated by the aid of the following relations;

$$\Delta E_{d_0-d_1} = (ch/2)[(\tilde{\nu}_{\mathrm{H--H}} - \tilde{\nu}_{\mathrm{H--D}}) - (\tilde{\nu}_{\mathrm{O-H}} - \tilde{\nu}_{\mathrm{O-D}})], \quad (1)$$

$$\Delta E_{d_1-d_4} = (ch/2)[(\tilde{\nu}_{\mathrm{H--D}} - \tilde{\nu}_{\mathrm{D--D}}) - (\tilde{\nu}_{\mathrm{C-H}} - \tilde{\nu}_{\mathrm{C-D}})], \quad (2)$$

$$\tilde{\nu} = (2\pi c)^{-1}(k_f/\mu)^{\frac{1}{2}}, \quad (3)$$

where ΔE is a difference in the activation energies, d_n means an alcohol containing n deuterium atoms per molecule, c is the velocity of light, h is the planck constant, $\tilde{\nu}$ is a wave number of the stretching vibration, k_f is a force constant and μ is a reduced mass.

The force constant for H--H (H--D, D--D) vibration was evaluated by assuming that the potential energy U nearest to its minimum U_0 is approximated by

$$U = U_0 + \tfrac{1}{2}k_f(r_4 - r_{4,0})^2 + \frac{1}{3!}a(r_4 - r_{4,0})^3, \quad (4)$$

where a is a constant. The comparison between the potential energy curve approximated by Eq. (4) and the true potential energy curve obtained from the vertical cross section of the potential energy surface (Fig. 3) at $r_5 = 1.297$ Å and $r_2 = 1.27$ Å (saddle point) is given in Fig. 6. Alternatively, k_f can be evaluated by using the Johnston's empirical relation (*13*) which re-

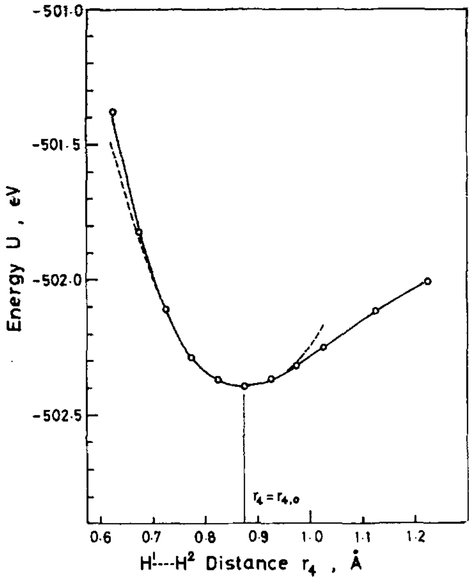

FIG. 6. Vertical cross section of the potential energy surface at $r_2 = 1.27$ Å and $r_5 = 1.297$ Å. (○) Calculated values by MINDO/2 method. (- - -) approximate potential energy curve by Eq. 4.

lates the H- -H bond length with k_f value. The results of calculation are given in Table 2.

Case 2. In the limiting case where H- -H mode is parallel to the reaction coordinate and both modes of O- -H¹ and C- -H² are orthogonal to the reaction coordinate, the theoretical kinetic isotope effects can be evaluated by the following relations;

$$\Delta E_{d_0-d_1} = (ch/2)[(\tilde{\nu}_{\text{O--H}} - \tilde{\nu}_{\text{O--D}}) - (\tilde{\nu}_{\text{O-H}} - \tilde{\nu}_{\text{O-D}}), \tag{5}$$

$$\Delta E_{d_1-d_4} = (ch/2)[(\tilde{\nu}_{\text{C--H}} - \tilde{\nu}_{\text{C--D}}) - (\tilde{\nu}_{\text{C-H}} - \tilde{\nu}_{\text{C-D}})]. \tag{6}$$

TABLE 2

EXPERIMENTAL AND THEORETICAL KINETIC ISOTOPE EFFECTS FOR THE DEHYDROGENATION OF METHYL ALCOHOL AT 475°C[a]

	Obsd	Calcd					
		k_f from Eq. (4)			k_f from Johnston's relation		
		(I_1)	(I_2)	(I)	(I_1)	(I_2)	(I)
X_{d_0}/X_{d_1}	1.74	1.74	1.58	1.68	1.68	1.58	1.64
X_{d_1}/X_{d_4}	1.37	1.29	1.42	1.34	1.24	1.42	1.31

[a] X: Conversion; d_0: CH_3OH; d_1: CH_3OD, d_4: CD_3OD. (I_1): isotope effects for Case 1; (I_2): isotope effects for Case 2; (I): overall isotope effects hybridized from (I_1) and (I_2).

In order to evaluate the force constants of the O- -H (O- -D) stretching vibration in the activated complex, the following relation (*14*) was employed;

$$F = F_s 10^{-(R-R_s)/0.6}, \tag{7}$$

where F_s is a force constant for O—H (O—D) single bond of length R_s (Å), F is a force constant for O- -H (O- -D) bond [the bond length is R (Å)] in the activated complex.

The force constant for the C- -H (C- -D) stretching vibration can be calculated in the same manner as above. The results of calculation are given in Table 2.

Hybridization of case 1 and case 2. The overall isotope effect (I) was hybridized from the isotope effect for the case 1 (I_1) and that for case 2 (I_2). The method of the hybridization employed in this work is very simple. Namely, the overall isotope effect I was expressed by the following relation:

$$I = C_1 I_1 + C_2 I_2, \tag{8}$$

where C_1 and C_2 are coefficients representing the respective contributions of the isotope effects for case 1 and case 2 to the overall isotope effect. Of course, $C_1 + C_2 = 1$. As shown in Fig. 3, the slope (chain line) of the reaction path (broken line) at the saddle point intercepts the r_4 axis at 1.65 Å while it intercepts the r_5 axis at 2.81 Å. Therefore, it was postulated that $C_1/C_2 = 2.81/1.65 = 1.7/1$. Since values of I_1 and I_2 were already obtained (Table 2), the overall isotope effect I can be evaluated by the aid of Eq. (8) and $C_1/C_2 = 1.7/1$. The results of hybridization are given in Table 2.

COMPARISON BETWEEN THE TWO-DIMENSIONAL AND THREE-DIMENSIONAL DEHYDROGENATION ISOTOPE EFFECTS

As shown in Table 2, the kinetic isotope effects observed in the dehydrogenation of methyl alcohol over the liquid indium are in agreement with the calculated values. This is an interesting result but care should be taken in interpreting it. Two extreme arguments concerning the implication of Table 2 seem to be possible.

In one extreme, the data given in Table 2 is considered to suggest that the three-dimensional unimolecular dehydrogenation pathway (I → II → III → IV) simulates well the two-dimensional unimolecular dehydrogenation (dehydrogenation over the liquid indium). It is assumed that the configuration of the activated complex (III) is conserved even after the adsorption, though certain effects of adsorption may appear on the other properties of the activated complex. The justification of this argument is given by the agreement between the isotope effects of the surface reaction and those of the gas phase reaction. According to this argument, the present SCF-MO calculation is considered to provide a limited but useful information about the surface reaction.

On the contrary, it is considered in the other extreme that the effect of adsorption would be significant and the configuration of the activated complex (III) may greatly be altered by the adsorption. Therefore, neither the three-dimensional pathway (I → II → III → IV) nor the activated complex model (Fig. 5) is considered to be available to simulate the surface reaction. In this argument, the agreements in the isotope effects in Table 2 are regarded to be fortuitous. Thus, according to this argument, the present SCF-MO treatment loses its standpoint in the analysis of the surface dehydrogenation of methyl alcohol.

In order to decide which of the two extreme arguments described above is adequate, effects of adsorption must be clarified. The adsorption energies of lower aliphatic alcohols are ~10 kcal/mol (*7*, *8*) and the adsorption energy ($Q_{ad}\ddagger$) of the activated complex (III) is calculated to be ~28 kcal/mol ($Q_{ad}\ddagger = E_0^b - E_{obs}$, where E_{obs} is an observed activation energy of the dehydrogenation of methyl alcohol over the liquid indium). Therefore, there is no question that the adsorption may alter the shape of the potential energy surface given in Fig. 3. This strengthens the latter argument. Nevertheless, the possibility of the conservation of the configuration of the activated complex cannot completely be denied. It seems to be adequate to consider that the implication of the data given in Table 2 is open to further studies.

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