The Mechanism of the Isotopic Exchange Reaction between Cyclohexane and Deuterium on Evaporated Metal Films*

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In recent years many improved theoretical treatments have been carried out to determine the mechanism of the catalytic hydrogenation and the exchange reaction of various olefinic and paraffinic hydrocarbons[1-6]. Refined theoretical treatments of the catalytic exchange reactions between cyclic hydrocarbons and deuterium on evaporated metal films have also been carried out by Anderson and Kemball[7]. In that work the probabilities of two kinds of multiple exchange were statistically calculated. In the case of cyclohexane, the first was the probability of exchanging alternately axial and equatorial hydrogen atoms in one group (i. e. three axial and three equatorial), and the second was the probability of turning over of the adsorbed radical by second-point adsorption. However, the discordance between the experimental and the calculated values of the initial product distributions was, in general, considerably predominant.

In the former papers[8,9] the authors have investigated the isotopic exchange reaction between cyclohexane and deuterium on evaporated films of molybdenum and tungsten. It was therefore of interest to study the theoretical treatments of this exchange reaction.

Outline of Theoretical Calculation

According to the experimental results and the kinetic consideration already reported in the former papers, it may be considered probable that the isotopic exchange reaction between cyclohexane and deuterium over evaporated films of molybdenum and tungsten proceeds with the following processes.

(1) Dissociative adsorption of deuterated hydrogen takes place on the metal surface. Adsorption and desorption of hydrogen lie in an equilibrium.

(2) Dissociative adsorption of cyclohexane also takes place on the metal surface. Adsorption and desorption of cyclohexane also lie in an equilibrium.

(3) The adsorbed " cyclohexyl " radical may be desorbed to the gas phase as " cyclohexane " (i. e. the single exchange process).

(4) Either by exchanging adjacent hydrogen atoms in one group or by turning over on the surface, the adsorbed " cyclohexyl " radical further migrates over the surface (i. e. the multiple exchange process).

According to Anderson and Kemball, the last process (4) may be termed a " trip ". However, as already discussed in the former papers[8,9], there is no definite experimental and geometrical reason to support the appearance of a marked discontinuity which separates the concentrations of $C_6H_6D_6$ and $C_6H_5D_7$. It matters little, therefore, for the present authors to distinguish the multiple exchange among adjacent hydrogen atoms

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[6] K. Miyahara, *J. Res. Inst. Catalysis*, **4**, 143 (1956).

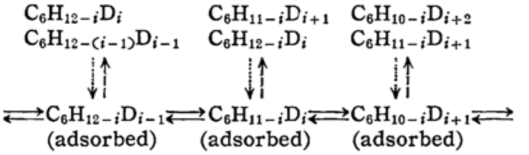
[7] J. R. Anderson and C. Kemball, *Proc. Roy. Soc.* (London), **A226**, 472 (1954).

[8] T. Hayakawa and T. Sugiura, This Bulletin, **31**, 180 (1958).

[9] T. Hayakawa and T. Sugiura, This Bulletin, **31**, 186 (1958).

in one group from that accompanied by the turning over of the adsorbed cyclohexyl radical on the surface.

From the reasons mentioned above, the present authors support the following reaction scheme, in which downward dotted lines, upward broken lines, and sideward full lines represent adsorption, desorption (i. e. the single exchange process) and tripping (i. e. the multiple exchange process) respectively.



In the present theoretical calculation, the following assumptions were made:

(1) At the initial stage of this exchange, the deuterium content of the adsorbed hydrogen atoms equals to that in the gas phase (i. e. hydrogen lies in an isotopic equilibrium).

(2) The adsorbed hydrogen atoms are randomly distributed on the metal surface.

(3) The deuterium isotope effect is negligible for each process shown in the reaction scheme.

Let V, the overall tripping rate of adsorbed cyclohexyl radicals, V', the overall rate of desorption (or dissociative adsorption) of cyclohexane, C_i, the surface concentration of the cyclohexyl-d_i ($i=0\sim11$) radical, C_i', the concentration of cyclohexane-d_i ($i=0\sim12$) in the gas phase, Q_i, the concentration ratio of the cyclohexyl-d_i radical to total cyclohexyl radicals on the surface, Q_i', the concentration ratio of cyclohexane-d_i to total cyclohexane molecules in the gas phase, and Ω, the ratio of the fraction covered by deuterium atoms to that by total hydrogen atoms.

The increasing rate of the surface concentration of the cyclohexyl-d_i radical and the gas phase concentration of cyclohexane-d_i are then given by the following Eqs. (1) to (4).

$$\begin{aligned} \mathrm{d}C_i/\mathrm{d}t = {} & V'\left(\frac{12-i}{12}Q_i'+\frac{i+1}{12}Q'_{i+1}\right) \\ & -V'Q_i+V\left\{\frac{12-i}{11}\Omega Q_{i-1}\right. \\ & -\frac{(11-i)\Omega+i(1-\Omega)}{11}Q_i \\ & \left.+\frac{i+1}{11}(1-\Omega)Q_{i+1}\right\},\quad i=1\sim10, \end{aligned} \tag{1}$$

$$\begin{aligned} \mathrm{d}C_{11}/\mathrm{d}t = {} & V'\left(\frac{1}{12}Q'_{11}+Q'_{12}\right) \\ & -V'Q_{11}+V\left\{\frac{1}{11}\Omega Q_{10}-(1-\Omega)Q_{11}\right\}, \end{aligned} \tag{2}$$

$$\mathrm{d}C_i'/\mathrm{d}t=V'\{(1-\Omega)Q_i+\Omega Q_{i-1}-Q_i'\},\quad i=1\sim11, \tag{3}$$

$$\mathrm{d}C'_{12}/\mathrm{d}t=V'(\Omega Q_{11}-Q'_{12}). \tag{4}$$

As reported in the work of Anderson and Kemball[7], the extent of multiple exchange may be defined in terms of a parameter P, the ratio of V to V'. At the steady state of this exchange reaction all $\mathrm{d}C_i/\mathrm{d}t$ ($i=1\sim11$) values tend to zero and at the initial stage of this exchange all $Q'_i(i=1\sim12)$ values may be negligible, so that Eqs. (1)$\sim$(4) become respectively

$$\begin{aligned} & P\left\{\frac{(12-i)\Omega}{11}\cdot\frac{Q_{i-1}}{Q_0}\right. \\ & \quad -\frac{(11-i)\Omega+i(1-\Omega)}{11}\cdot\frac{Q_i}{Q_0} \\ & \quad \left.+\frac{(i+1)(1-\Omega)}{11}\cdot\frac{Q_{i+1}}{Q_0}\right\}-\frac{Q_i}{Q_0}=0, \\ & \qquad i=1\sim10, \end{aligned} \tag{5}$$

$$P\left\{\frac{\Omega}{11}\cdot\frac{Q_{10}}{Q_0}-(1-\Omega)\frac{Q_{11}}{Q_0}\right\}-\frac{Q_{11}}{Q_0}=0, \tag{6}$$

$$\mathrm{d}C'_i/\mathrm{d}t=V'Q_0\left\{(1-\Omega)\frac{Q_i}{Q_0}+\Omega\frac{Q_{i-1}}{Q_0}\right\},\quad i=1\sim11, \tag{7}$$

$$\mathrm{d}C'_{12}/\mathrm{d}t=V'Q_0\cdot\Omega\frac{Q_{11}}{Q_0}. \tag{8}$$

Since assumption (1) indicates that at the initial stage of this exchange Ω stays in a constant value*, one can obtain each $Q_i/Q_0(i=1\sim11)$ value for each given value of P by solving Eqs. (5)$\sim$(6). Then, by inserting each Q_i/Q_0 value thus obtained in Eqs. (7)$\sim$(8), one can calculate the relative values of $\mathrm{d}C'_i/\mathrm{d}t(i=1\sim12)$ at the initial stage of this exchange.

Results

The present results on the theoretical distributions of the initial products as functions of $\log P$ are shown in Fig. 1. The theoretical values of the percentage distributions of the initial products at various temperatures over evaporated films of molybdenum and tungsten are

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* As already reported in the former papers[8,9], the experimental value of Ω was 0.361. In the present theoretical calculation, however, the value of Ω was taken as 1/3 to facilitate calculations.

TABLE I

PERCENTAGE DISTRIBUTIONS OF INITIAL PRODUCTS ON EVAPORATED MOLYBDENUM FILMS

Temp. (°C)	P		$d(C_6H_{12-i}D_i)/dt$							
			$i=1$	2	3	4	5	6	7	8
75	6	calcd.	40.2	27.8	17.1	9.0	4.1	1.4	0.4	—
		obsd.	41.0	26.4	15.8	10.5	4.2	2.1	—	—
86.5	9	calcd.	32.3	26.6	19.3	12.2	6.3	2.5	0.8	—
		obsd.	32.4	24.8	20.2	12.1	6.5	4.0	—	—
97	10.5	calcd.	30.1	25.8	20.1	12.1	7.2	3.4	1.2	0.1
		obsd.	30.4	24.1	17.4	12.5	7.9	5.3	2.4	—
102	13	calcd.	26.5	24.6	20.8	14.6	8.3	3.6	1.3	0.3
		obsd.	26.2	22.2	20.2	15.7	7.0	4.9	3.8	—

TABLE II

PERCENTAGE DISTRIBUTIONS OF INITIAL PRODCUTS ON EVAPORATED TUNGSTEN FILMS

Temp. (°C)	P		$d(C_6H_{12-i}D_i)/dt$						
			$i=1$	2	3	4	5	6	7
84	2.8	calcd.	56.3	26.5	11.2	4.2	1.4	0.4	—
		obsd.	57.2	25.3	9.2	5.8	1.9	0.6	—
94	3.8	calcd.	50.2	27.6	13.6	5.8	2.1	0.7	—
		obsd.	51.7	27.0	11.9	6.0	2.4	1.0	—
102	5.8	calcd.	40.6	28.2	17.0	8.7	3.8	1.4	0.3
		obsd.	40.6	26.0	19.6	7.8	4.5	1.2	0.3
111	7.4	calcd.	36.3	27.5	18.4	10.6	4.9	1.8	0.5
		obsd.	36.3	26.9	18.2	11.8	5.1	1.3	0.4

TABLE III

ACTIVATION ENERGY DIFFERENCES AND FREQUENCY FACTOR RATIOS

Catalyst	E(tripping) − E(desorption) (kcal./mol.)	$\frac{A\text{(tripping)}}{A\text{(desorption)}}$	Temp. range (°C)
Molybdenum films	6.8	1.15×10^5	75 to 102
Tungsten films	9.7	2.43×10^6	84 to 111

TABLE IV

ACTIVATION ENERGIES

Catalyst	E(desorption) (kcal./mol.)	E(tripping) (kcal./mol.)	Temp. range (°C)
Molybdenum films	$9.8+(-\Delta H)$	$16.6+(-\Delta H)$	75 to 102
Tungsten films	$10.3+(-\Delta H)$	$20.0+(-\Delta H)$	84 to 111

summarized in Tables I and II, together with the observed values by the present authors[8,9]. Arrhenius plots of P values are given in Fig. 2. The differences between the activation energy of tripping and that of desorption (or chemisorption) for these evaporated films are listed in Table III, together with the ratios of the frequency factor of tripping to that of desorption (or chemisorption).

Discussion

Initial Product Distributions.—In spite of the fact that the value of Ω used in the present theoretical calculations was slightly different from that experimentally found, the agreements between the theoretical and the experimental values of the initial product distributions for these metal films shown in Tables I and II are well maintained. This is attributed to the fact that the theoretical distributions shown in Fig. 1 were practically unchanged by a slight difference in the value of Ω. Refined statistical calculations of the initial product distributions for the same exchange reaction have been carried out by Anderson and Kemball[7]. However, the discrepancies between the theoretical and the experimental values were considerably predominant except for the results on palladium films at 44°C. The incompleteness of their theoretical treatments may be mainly attributed to the fact that the steady state conditions were not taken into consideration.

Mechanism of the Present Exchange

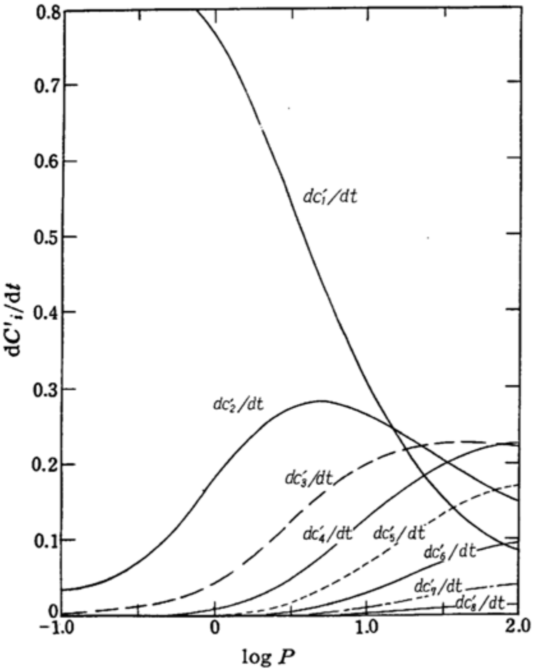

Fig. 1. Theoretical distributions of initial products as functions of log P. dC'_i/dt is fraction of initial rate of increase of cyclohexane-d_i.

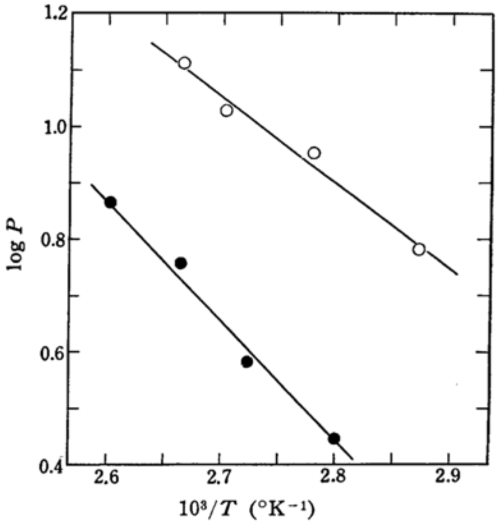

Fig. 2. Arrhenius plot of P values.
—○—○—, on evaporated molybdenum films;
—●—●—, on evaporated tungsten films.

Reaction. — As already discussed in a preceding paper[8], the rate-determining step of this exchange reaction may be the desorption of the cyclohexyl radicals. This coincides well with the fact that, as seen in Tables I and II, the theoretical values of P at various temperatures are considerably greater than unity. Since, as described in a preceding paper[8], the apparent activation energy experimentally found for this exchange would imply the activation energy of chemisorption of cyclohexane, one can obtain the activation energy for each process by combining the present theoretical calculations with the experimental results already reported in the fomer papers[8,9]. The present results on these activation energies are summarized in Table IV, where $(-\Delta H)$ denotes the heat of chemisorption of cyclohexane.

Summary

The theoretical treatments of the isotopic exchange reaction between cyclohexane and deuterium over evaporated metal films have been studied. The present results of the theoretical calculations were compared with the experimental results already obtained by the present authors for evaporated films of molybdenum and tungsten. The present results are summarized as follows:

1) The agreements between the theoretical and the experimental values of the initial product distributions for these metal films are well maintained.

2) The initial rate of tripping of the adsorbed radicals on evaporated films of molybdenum or tungsten at each temperature is considerably greater than that of desorption (or chemisorption) of cyclohexane. This coincides well with the experimental fact that the rate-determining step of this exchange reaction may be attributed to desorption of the adsorbed radicals.

3) The differences between the activation energy of tripping of the adsorbed radicals and that of desorption for evaporated films of molybdenum and tungsten amount to 6.8 and 9.7 kcal./mol. respectively.

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