Isotopic Exchange Reaction between Cyclohexane and Deuterium on Evaporated Molybdenum Films[*]

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Catalytic exchange reactions between cyclic hydrocarbons and deuterium have been the subject of recent investigations. The exchange reaction between cyclohexane and deuterium on evaporated metal films has been studied by Anderson and Kemball[1]. Their results on rhodium and palladium clearly indicated that half of the hydrogen atoms were readily exchanged. For the remaining six hydrogen atoms to be exchanged, they proposed the mechanism in which the adsorbed radical turns over on the surface by second-point adsorption. Although their multiple exchange mechanism is very efficient, the discordance between the experiments and the theoretical calculations based on this mechanism for the initial product distributions was considerably predominant.

The exchange reaction between cyclohexane and deuterium over various nickel catalysts have also been reported by Burwell et al[2,3]. According to their results, no discontinuities which separate the concentrations of $C_6H_6D_6$ and $C_6H_5D_7$ appeared at 160–200°C when evaporated nickel films or reduced nickel oxide were used. In recent years we have also investigated the isotopic exchange reaction between cyclohexane and deuterium on evaporated metal films, since it was of interest to clarify the mechanism of this exchange and the contribution of the deuterium isotope effect.

Experimental

Materials.—Wako Chemicals Pure Grade *cyclohexane* was purified by several fractionations and dissolved gases were removed by pumping under vacuum while chilled. *Deuterated hydrogen* was prepared from complete decomposition of heavy water over pure metallic sodium preliminary outgassed and distilled in vacuo; it was purified by passing through traps cooled in liquid nitrogen under the reduced pressure and then by passing through a sodium-gettered glass tube.

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[*] A part of this paper was read before the 9th Annual Meeting of the Chemical Society of Japan held in Kyoto, April, 1956. Another part of this paper was also presented before the "Symposium on the Catalytic Reactions" held in Tokyo, April, 1957.

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

2) H. C. Rowlinson, R. L. Burwell, Jr. and R. H. Tuxworth, *J. Phys. Chem.*, **59**, 225 (1955).

3) R. L. Burwell, Jr. and R. H. Tuxworth, ibid., **60**, 1043 (1956).

The mass spectrometric analyses revealed that the deuterium content of this sample was 36.1 atomic %.

Evaporated Molybdenum Films.—Evaporated molybdenum films were prepared by customary procedures including careful degassing at elevated temperatures. The reaction vessel was a cylindrical glass tube (inside diameter 30 mm., length about 20 cm.) and between 5.1 and 10.9 mg. of molybdenum was evaporated onto the inner surface of this tube while the tube was cooled in ice water. After each experiment the weight of evaporated films was determined by the usual volumetric analysis.

Apparatus and Procedure.—The principal diagram of the apparatus is shown in Fig. 1.

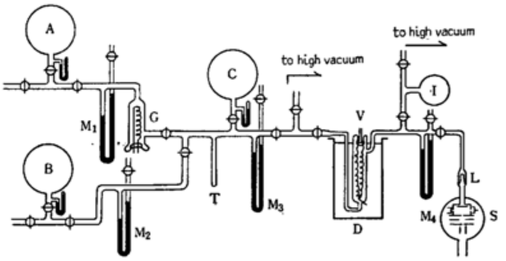

Fig. 1. Principal diagram of the apparatus.

Reservoir A containing purified deuterated hydrogen was connected to a sodium-gettered valve G by which the trace quantity of oxygen or water vapor was removed. The bulb B shows a reservoir of purified cyclohexane vapors, M_1 and M_2 auxiliary mercury manometers. T shows a trap cooled in liquid nitrogen, by which cyclohexane vapors were chilled before mixing. The sample gases were premixed and introduced into the storage bulb C, and the composition of each gas mixture was determined by means of the mercury manometer M_3.

Before commencing each experiment, the reaction vessel V was thoroughly evacuated for several hours and molybdenum was evaporated onto the inner surface of this vessel (the high vacuum was measured by means of the ionization gauge I). Then the reaction vessel was heated and controlled to the required temperature by means of the oil-bath thermostat D; the sample gases were admitted into the reaction vessel and the pressure was measured by means of the mercury manometer M_4. The oil-bath thermostat was operated by the usual electrical relay circuit; the temperature variation recorded by this thermostat was never greater than ± 0.1°C. After a given time, the gases were introduced, through the gas leak L, into the ion source S of a mass spectrometer and the product-compositions were determined. Since the orifice diameter of the gas leak was very small (i. e. smaller than 0.01 mm.), the pressure in the reaction vessel was practically unchanged.

In the present experiments, mass spectrometric analyses were performed on a modified Hitachi RMC mass spectrometer (90° sector type, the radius of curvature of the ion path and the maximum mass resolution were 135 mm. and about 150, respectively). The recording time required for magnetic scanning in the mass range between $m/e=83$ and 96 was about one minute, and other details of this instrument were already given[4]. For cyclohexane, 30 V. electrons were used for ionization, and at this ionizing voltage only a small fragmentation correction was required owing to the production of 6 % of the ion formed by the loss of one hydrogen atom. Corrections for fragmentation were made by assuming that the probability of ionization in the mass spectrometer was independent of isotopic content. Corrections were also made for deuterium and heavy carbon (C^{13}) occurring naturally in cyclohexane.

Results

The experimental conditions are shown in Table I, where the run numbers indicate the chronological order of the experiments. Figs. 2-6 show some typical results on the variation in the percentage of the various cyclohexane molecules with time. In these figures, the notation d_i has been used in place of cyclohexane-d_i ($C_6H_{12-i}D_i$) to facilitate presentation. Typical results on the initial product distributions obtained from measuring the initial slopes of these curves are also listed in Table II.

TABLE I

DETAILS OF ISOTOPIC EXCHANGE RUNS

Run	Temp. (°C)	Partial pressure (mmHg)	
		cyclohexane	deuterated hydrogen
7	111	15.4	15.4
8	75	15.5	15.5
9	97	19.6	19.6
11	56	11.4	11.4
12	102	10.1	10.1
13	86.5	14.8	14.8
14	75	6.8	6.8
15	106	9.0	9.0
16	102	6.9	6.9
17	87	6.7	6.7
18	86.5	6.8	6.8
21	75	20.4	5.1
22	94	3.0	2.0
23	102.5	1.5	1.0
24	97	7.5	7.5
28	97	6.5	6.5
29	97	12.8	6.4
30	97	18.9	6.3
31	97	24.3	6.1

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[4] T. Hayakawa and T. Sugiura, *Bull. Naniwa Univ., Series A*, **3**, 193 (1955).

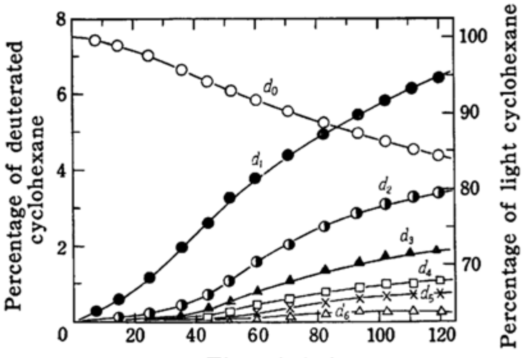

Fig. 2. The exchange of cyclohexane on 6.8 mg. of molybdenum at 75°C (run 14).

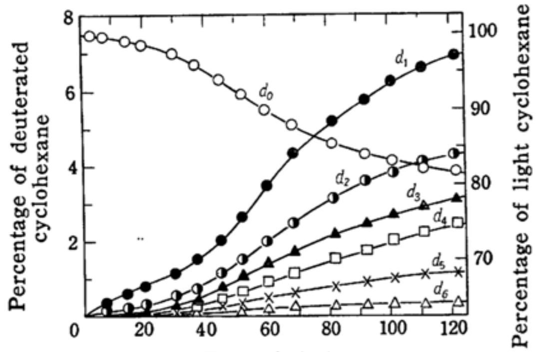

Fig. 3. The exchange of cyclohexane on 6.7 mg. of molybdenum at 86.5°C (run 18).

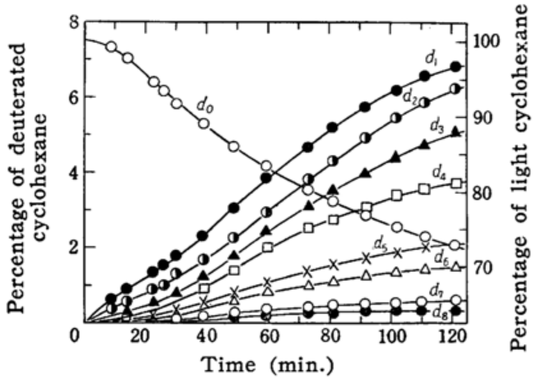

Fig. 4. The exchange of cyclohexane on 8.1 mg. of molybdenum at 102°C (run 16).

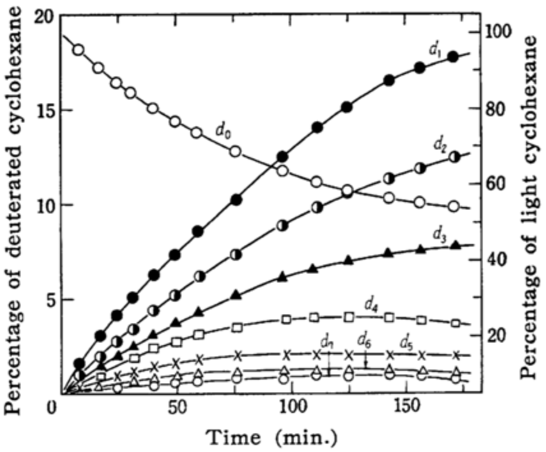

Fig. 5. The exchange of cyclohexane on 9.9 mg. of molybdenum at 97°C (run 29).

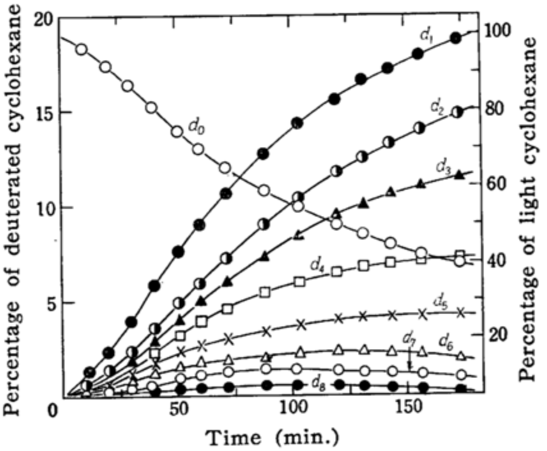

Fig. 6. The exchange of cyclohexane on 5.0 mg. of molybdenum at 97°C (run 31).

TABLE II

PERCENTAGE DISTRIBUTION OF INITIAL PRODUCTS (Equimolecular mixtures)

Initial rate	Temperature (°C)			
	75 (run 14)	86.5 (run 18)	97 (run 28)	102 (run 16)
$d(C_6H_{11}D)/dt$	41.0	32.4	30.4	26.2
$d(C_6H_{10}D_2)/dt$	26.4	24.8	24.1	22.2
$d(C_6H_9D_3)/dt$	15.8	20.2	17.4	20.2
$d(C_6H_8D_4)/dt$	10.5	12.1	12.5	15.7
$d(C_6H_7D_5)/dt$	4.2	6.5	7.9	7.0
$d(C_6H_6D_6)/dt$	2.1	4.0	5.3	4.9
$d(C_6H_5D_7)/dt$	—	—	2.4	3.8

As described in the works of Anderson and Kemball[1,5], two different rates were determined from each experiment. The variation in the percentage (n) of light cyclohexane with time followed the equation

$$-\log(n-n_\infty)=\frac{k_H t}{2.303(100-n_\infty)}+\text{constant}, \tag{1}$$

where n_∞ represents the equilibrium value of n and k_H the initial rate of disappear-

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[5] J. R. Anderson and C. Kemball, *Proc. Roy. Soc.* (London), **A223**, 361 (1954).

ance of light cyclohexane in percent. per unit time. For cyclohexane ϕ was defined

$$\phi = \sum_i i \times N_i, \qquad (2)$$

where N_i denotes the percentage of cyclohexane-d_i ($C_6H_{12-i}D_i$, $i=1\sim12$) at the given time. The variation of ϕ with time also followed the equation

$$-\log(\phi_\infty - \phi) = \frac{k_D t}{2.303\phi_\infty} + \text{constant}, \qquad (3)$$

where ϕ_∞ was the equilibrium value of ϕ and k_D the initial rate of entry of deuterium atoms into cyclohexane expressed as the number of deuterium atoms entering 100 cyclohexane molecules in unit time.

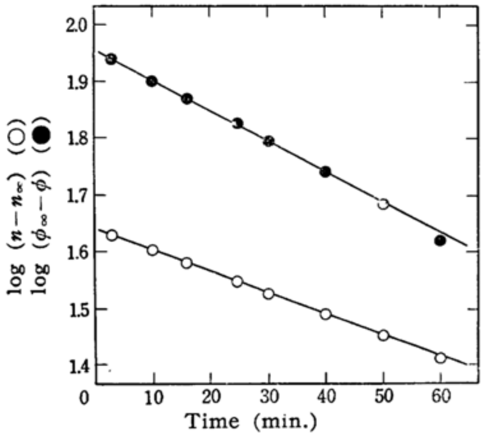

Fig. 7. The exchange of cyclohexane on 5.7 mg. of molybdenum at 97°C plotted according to the rate law expressions (run 28).

TABLE III

INITIAL RATES

(Equimolecular mixtures)

	Temperature (°C)			
	75 (run 14)	86.5 (run 18)	97 (run 28)	102 (run 16)
k_D(%/min.10mg.)	0.705	1.077	1.545	1.922
k_H(%/min.10mg.)	0.309	0.387	0.501	0.556
k_D/k_H	2.28	2.78	3.17	3.46

Fig. 7 shows typical results plotted according to Eqs. (1) and (3). The values of k_H and k_D at various temperatures are summarized in Table III in which the weight of evaporated films was normalized to 10 mg. Arrhenius plots are given in Fig. 8 and the apparent activation energies and the frequency factors in Table IV.

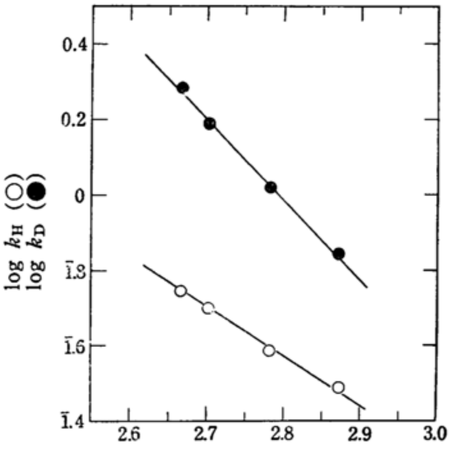

Fig. 8. The effect of temperature on the initial rates of exchange of cyclohexane on molybdenum. k_H and k_D in %/min.10 mg.

TABLE IV

APPARENT ACTIVATION ENERGIES (E) AND FREQUENCY FACTORS (A)

	E(kcal. /mol.)	A(mol./min. 10 mg.)	Temp. range(°C)
k_D plot	9.8	7.05×10^{10}	75 to 102
(k_H plot)	(6.2)	(1.10×10^{8})	(75 to 102)

Discussion

Distributions of the Exchange Products.—Considering the fact that the deuterium content of hydrogen in our experiments was only 36.1 atomic %, the production of considerable amounts of highly deuterated products, as seen in Figs. 2–6 and Table II, requires a process of multiple exchange. Anderson and Kemball(1) have reported that isotopic exchange between cyclohexane and deuterium on evaporated films of rhodium (−48 and −28°C) and palladium (18.5°C) leads to distribution patterns in which marked discontinuities separate the concentrations of $C_6H_6D_6$ and $C_6H_5D_7$. On the other hand, Burwell and Tuxworth(3) have reported that at 160–200°C no such discontinuities between $C_6H_6D_6$ and $C_6H_5D_7$ appeared when evaporated nickel films or reduced nickel oxide were used. As seen in Figs. 2–6 and Table II, the present results clearly indicate that at 75–102°C one can observe no discontinuities between $C_6H_6D_6$ and $C_6H_5D_7$ for molybdenum films.

It is well known that both in the liquid and the vapor all cyclohexane molecules are practically present in the chair form,

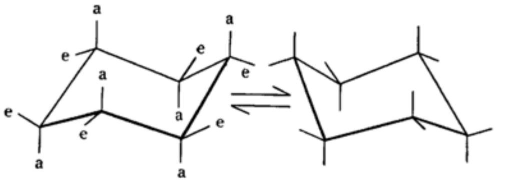

Fig. 9. The chair conformation of cyclohexane. The axial and equatorial bonds are marked (a) and (e) respectively.

as shown in Fig. 9, in which the twelve C–H bonds may be divided into two geometrically different groups of six equatorial (e) and six axial (a)[6]. Furthermore, owing to the flexibility of this chair conformation the two planes (i. e. each plane contains three carbon atoms) may interchange their positions, and all C–H bonds which were axial in the former chair form will be equatorial in the latter, and vice versa[7]. Based on this chair conformation mentioned above, a suggestion has been made by Anderson and Kemball that the reaction easily proceeds by exchanging alternately axial and equatorial hydrogen atoms in one group of three axial and three equatorial and that, for the remaining six hydrogen atoms to be exchanged, the adsorbed radical must turn over on the surface by second-point adsorption. Marked discontinuities between $C_6H_6D_6$ and $C_6H_5D_7$ found by them over evaporated films of rhodium and palladium were attributed to the small probability of this turning over of the adsorbed radicals.

Their explanations, however, contain some uncertainties, since dissociative adsorption of desorbed cyclohexane molecules ($C_6H_{12-i}D_i$, $i<7$) may take place with the same probability of the rupture of a C–H bond on either side of the carbon ring. Moreover, when an adsorbed radical takes an inclined position towards the surface, exchange may proceed between adjacent equatorial hydrogen atoms within different groups and the radical may easily turn over on the surface. Considering the matter from these facts, it seems rather reasonable to consider that there are no definite reasons to support the appearance of a marked discontinuity which separates the concentrations of $C_6H_6D_6$ and $C_6H_5D_7$.

Pressure-Dependence of Reaction Rate.—According to the present experiments, the initial rates of this exchange were found to follow

$$k_D(\text{or } k_H) \propto p(C_6H_{12})^{1.0}\cdot p(\text{d.h.})^{-0.6}, \tag{4}$$

where p(d.h.) denotes the partial pressure of deuterated hydrogen. The uncertainty in the exponents amounts to about 0.1.

The non-activated chemisorption of hydrogen on various metal films has been reported by many investigators[8]; then one can easily deduce the following kinetic relation by assuming that the coverage of the mobile layer of the adsorbed radicals is considerably smaller than that of chemisorbed hydrogen atoms and that the initial rate (k) of this exchange is proportional to the amount of the adsorbed radicals.

$$k \propto \frac{p(C_6H_{12})}{\sqrt{b}\,p(\text{d.h.})^{0.5}+b\,p(\text{d.h.})^{1.0}}, \tag{5}$$

where b indicates the constant which characterizes adsorption and desorption of hydrogen, and p(d.h.) the partial pressure of deuterated hydrogen. Since Eq. (5) indicates that the initial rate is proportional to $p(\text{deuterated hydrogen})^{-1.0\sim-0.5}$, the present results shown in Eq. (4) and those obtained by Anderson and Kemball* approximately coincide with Eq. (5). It may, therefore, be considered probable that the rate-determining step of this exchange is desorption of the adsorbed radicals. On account of the fact that the deuterium content in our experiments was considerably small, the apparent activation energy derived from Arrhenius plot of k_D values is significant. Hence the value of 9.8 kcal./mol. shown in Table IV would imply the activation energy of dissociative adsorption of cyclohexane.

Deuterium Isotope Effect.—In order to examine the influence of the deuterium isotope effect, the compositions in equilibrated mixtures were determined both for the gas phase and for the gases newly desorbed from the surface after rapid evacuation. Typical results are summarized in Table V. Since only a minute quantity of the gases was newly desorbed, the present analytical results on the minor components in newly desorbed gases inevitably contain considerable uncertainties. Considering the problem from this fact, it seems reasonable to consider that, so far as the present experiments

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[6] O. Hassel, *Quart. Rev.*, **7**, 221 (1953).

[7] W. G. Dauben and K. S. Pitzer, "Steric Effects in Organic Chemistry", John Wiley & Sons, Inc., New York (1956), p. 17.

[8] M. W. Trapnell, "Chemisorption", Butterworths Scientific Publications, London (1955), p. 60.

* The pressure-dependence for this exchange over evaporated palladium films was found by them to follow $k_H \propto p(C_6H_{12})^{0.8}\cdot p(D_2)^{-1.0}$.

TABLE V
PERCENTAGE COMPOSITIONS OF EQUILIBRATED MIXTURES

Temp. (°C)	Sample	C_6H_{12}	$C_6H_{11}D$	$C_6H_{10}D_2$	$C_6H_9D_3$	$C_6H_8D_4$	$C_6H_7D_5$	$C_6H_6D_6$
94	Gas phase	60.9	28.7	7.5	1.7	0.8	0.4	—
	Newly desorbed gases	61.3	28.8	7.2	1.5	0.9	0.3	—
102	Gas phase	58.1	26.1	9.9	3.6	1.5	0.6	0.2
	Newly desorbed gases	57.4	26.4	9.8	3.8	1.7	0.6	0.3
111	Gas phase	54.7	22.9	12.2	6.1	2.7	0.9	0.5
	Newly desorbed gases	55.1	21.8	12.7	6.5	2.4	1.1	0.4

were concerned, the deuterium isotope effect gives no significant influence upon the overall reaction of this exchange.

Summary

Isotopic exchange reaction between cyclohexane and deuterium over evaporated molybdenum films has been studied mass-spectrometrically at the temperature range 56–111°C. The present results were compared either with Anderson and Kemball's or Burwell and Tuxworth's, and summarized as follows;

1) Since the deuterium content in our experiments was considerably low the production of considerable amounts of highly deuterated products requires a process of multiple exchange.

2) The present results clearly indicate that one can observe no discontinuities which separate the concentrations of $C_6H_6D_6$ and $C_6H_5D_7$.

3) The pressure-dependence was studied for this exchange and the initial rate (k) was found to be expressed as $k \propto p(C_6H_{12})^{1\cdot 0} \cdot p(\text{deuterated hydrogen})^{-0\cdot 6}$.

4) According to the present kinetic evidence, the rate-determining step of this exchange is probably the desorption of the cyclohexyl radicals.

5) So far as the present experiments were concerned, it seems reasonable to consider that the deuterium isotope effect gives no significant influence upon the present exchange reaction.

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