*Isotopic Exchange Reaction between Cyclohexane and Deuterium on Evaporated Tungsten Films**

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In the previous communication[1], the authors studied the isotopic exchange reaction between cyclohexane and deuterium over evaporated molybdenum films. It was found that the initial production of highly deuterated products required a process of multiple exchange. No discontinuites which separate the concentrations of $C_6H_6D_6$ and $C_6H_5D_7$ appeared at 56—111°C and the deuterium isotope effect practically gave no significant influence upon the exchange reaction. The pressure-dependence for this exchange and simple kinetic consideration revealed that the rate-determining step may be attributed to desorption of the chemisorbed radicals and hence that the apparent activation energy experimentally found would imply the activation energy of dissociative adsorption of cyclohexane.

It was therefore of interest in the present work to study the same exchange reaction over evaporated tungsten films, since this permits a comparison of the catalytic activities of these metal films.

Experimental

Materials.—The method of preparation and purification of the sample gases was already given in a previous communication[1]. Evaporated tungsten films were prepared by customary procedures including careful degassing at elevated temperatures. Between 7.9 and 16.4 mg. of evaporated film was used in the subsequent experiments.

Apparatus and Procedure.—The apparatus and the procedure were described in the previous communication[1].

Results

The experimental conditions are summarized in Table I, where the run numbers indicate the chronological order of the experiments. Figs. 1, 2 and 3 show some typical results on the variation in the percentages of the various cyclohexane molecules with time. In these figures the notation d_i has been used in place of cyclohexane-d_i

TABLE I

DETAILS OF ISOTOPIC EXCHANGE RUNS

Run	Temp. (°C)	Partial pressures (mmHg) cyclohexane	Partial pressures (mmHg) deuterated hydrogen
2	94	2.0	2.0
5	111	2.0	2.0
6	98.5	2.2	2.2
8	80	2.7	2.7
9	86	1.9	1.9
10	102	2.1	2.1
12	79	1.5	1.5
15	84	2.2	2.2

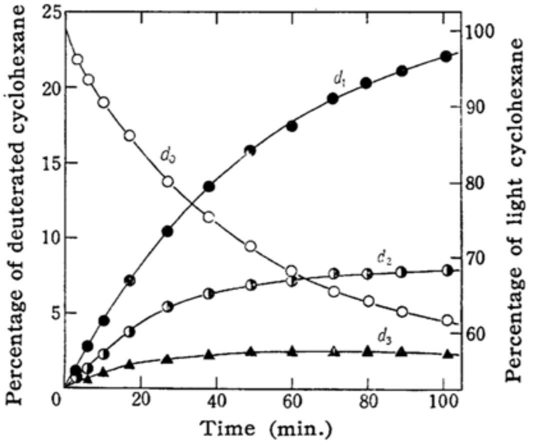

Fig. 1 (a). The exchange of cyclohexane on 12.4 mg. of tungsten at 84°C (run 15, major components).

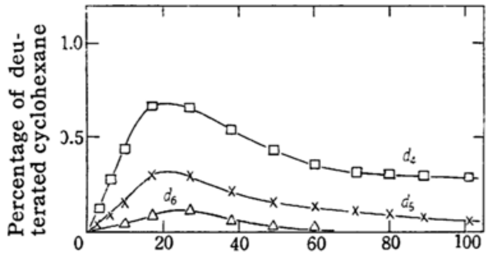

Fig. 1 (b). The exchange of cyclohexane on 12.4 mg. of tungsten at 84°C (run 15, minor components).

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* Part of this paper was read before the 10th Annual Meeting of the Chemical Society of Japan held in Tokyo, April, 1957. Another part of this paper was also presented before the Symposium on the Catalytic Reactions held in Tokyo, April, 1957.

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

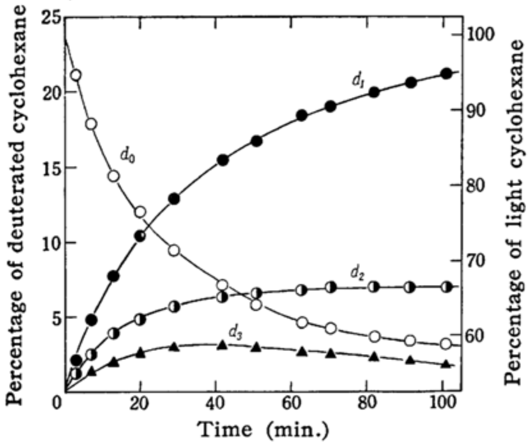

Fig. 2 (a). The exchange of cyclohexane on 16.4 mg. of tungsten at 94°C (run 2, major components).

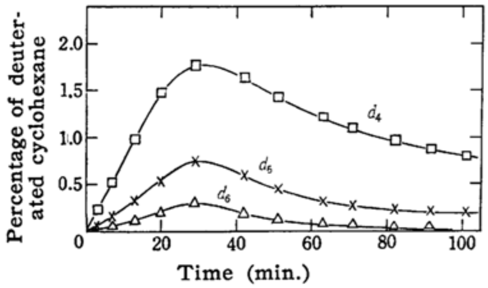

Fig. 2 (b). The exchange of cyclohexane on 16.4 mg. of tungsten at 94°C (run 2, minor components).

TABLE II

PERCENTAGE DISTRIBUTIONS OF INITIAL PRODUCTS

	Temperature (°C)			
Initial rate	84	94	102	111
$d(C_6H_{11}D)/dt$	57.2	51.7	40.6	36.3
$d(C_6H_{10}D_2)/dt$	25.3	27.0	26.0	26.9
$d(C_6H_9D_3)/dt$	9.2	11.9	19.6	18.2
$d(C_6H_8D_4)/dt$	5.8	6.0	7.8	11.8
$d(C_6H_7D_5)/dt$	1.9	2.4	4.5	5.1
$d(C_6H_6D_6)/dt$	0.6	1.0	1.2	1.3
$d(C_6H_5D_7)/dt$	—	—	0.3	0.4

TABLE III

INITIAL RATES

(Equimolecular mixtures)

	Temperature (°C)			
	84	94	102	111
k_D(%/min. 10 mg.)	1.175	1.682	2.281	3.116
k_H(%/min. 10 mg.)	0.742	1.006	1.208	1.611
k_D/k_H	1.58	1.68	1.89	1.93

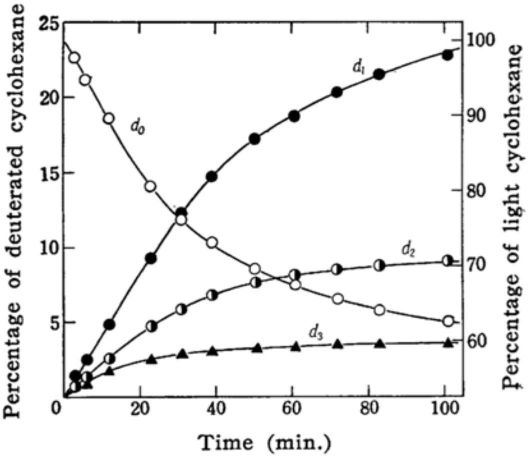

Fig. 3 (a). The exchange of cyclohexane on 9.9 mg. of tungsten at 102°C (run 10, major components).

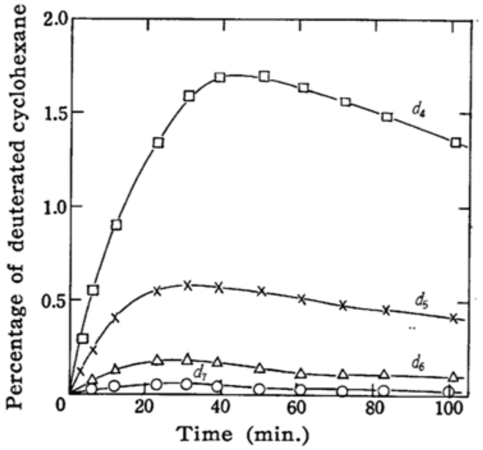

Fig. 3 (b). The exchange of cyclohexane on 9.9 mg. of tungsten at 102°C (run 10, minor components).

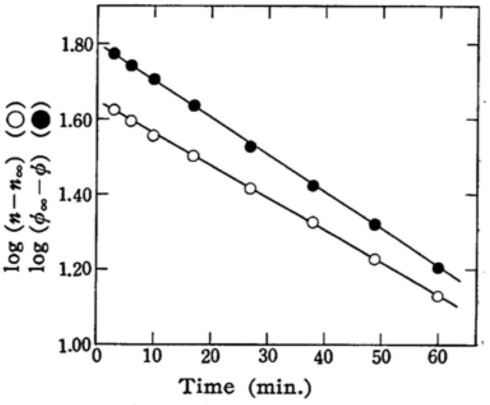

Fig. 4. The exchange of cyclohexane on 12.4 mg. of tungsten at 84°C plotted according to the rate law expressions (run 15).

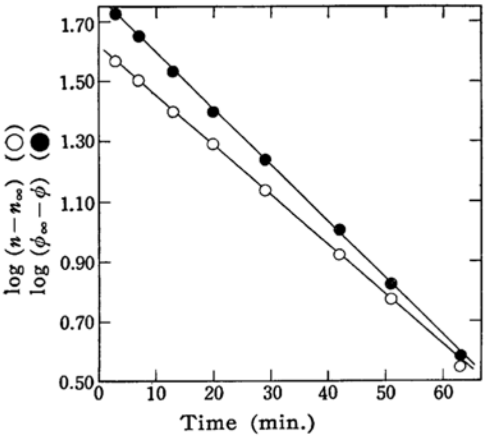

Fig. 5. The exchange of cyclohexane on 16.4 mg. of tungsten at 94°C plotted according to the rate law expressions (run 2).

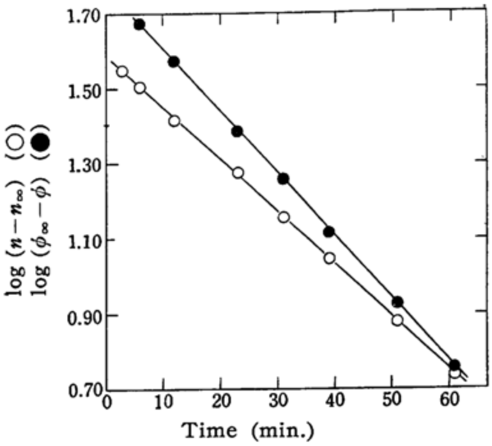

Fig. 6. The exchange of cyclohexane on 9.9 mg. of tungsten at 102°C plotted according to the rate law expressions (run 10).

($C_6H_{12-i}D_i$) to facilitate presentation. Typical results on the initial product distributions obtained from measuring the initial slopes of these curves are summarized in Table II. Two different rates, i. e. the initial rate of disappearance of light cyclohexane (k_H) and the initial rate of entry of deuterium atoms into cyclohexane (k_D), were calculated from the plot of the rate law expressions reported in the preceding paper[1]. Figs. 4, 5 and 6 show typical results plotted according to these expressions. The values of two different rates 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. 7 and the apparent activation energies and frequency factors in Table IV, together with the values obtained by Anderson and Kemball[2].

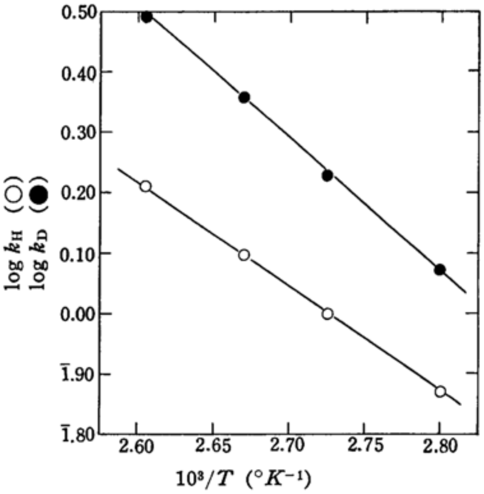

Fig. 7. The effect of temperature on the initial rates of exchange of cyclohexane on tungsten. k_H and k_D in %/min. 10 mg.

TABLE IV

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

	E (kcal. /mol.)	A (mol./min. 10 mg.)	Temp. range (°C)
k_D plot	10.3	7.43×10^{11}	84 to 111
(k_H plot)	(7.9)	(8.80×10^{9})	(84 to 111)
Anderson and Kemball* (k_H plot)	11	4.76×10^{28}	−69 to −48

* The initial deuterium content was 99.7%.

Discussion

Distributions of the Exchange Products.—As seen in Figs. 1∼3, considerable amounts of highly deuterated products appeared in the early stage of this reaction. Since the deuterium content of hydrogen in our experiments was only 36.1 atomic %, it is quite reasonable to consider that the process of multiple exchange plays a significant role in the present exchange reaction. These figures clearly indicate that increased temperature results in a marked increase in extensive multiple exchange. Comparing the present product distributions shown in Table II with those already reported in the preceding paper[1], it is obvious that the multiple exchange is more extensive on molybdenum films than on tungsten films.

As seen in Figs. 1∼3 and Table II, although decreased temperature results in the decline in concentrations of highly deuterated products, at 84—111°C one can observe no discontinuity which separates the concentrations of $C_6H_6D_6$ and $C_6H_5D_7$.

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

TABLE V

PERCENTAGE COMPOSITIONS OF EQUILIBRATED MIXTURES

Temp. (°C)	Sample	C_6H_{12}	$C_6H_{11}D$	$C_6H_{10}D_2$	$C_6H_9D_3$	$C_6H_8D_4$	$C_6H_7D_5$
84	Gas phase	60.1	29.6	8.2	1.8	0.3	—
	Newly desorbed gases	60.7	29.4	7.9	1.5	0.5	—
94	Gas phase	56.9	30.9	8.7	2.7	0.8	—
	Newly desorbed gases	57.4	30.6	8.2	2.8	1.0	—
102	Gas phase	58.1	25.8	10.9	3.5	1.3	0.4
	Newly desorbed gases	56.2	26.7	10.9	4.1	1.5	0.6

These results closely resemble those already found for evaporated molybdenum films. Moreover, no such discontinuities between $C_6H_6D_6$ and $C_6H_5D_7$ have been observed either by Anderson and Kemball[2] for evaporated films of platinum (at 0°C) and tungsten (at −69°C) nor by Burwell and Tuxworth[3] for evaporated nickel films (at 160—200°C). From these facts, it seems reasonable for the present authors to consider that marked discontinuities between $C_6H_6D_6$ and $C_6H_5D_7$ observed by Anderson and Kemball[2] for evaporated films of rhodium (at −48 and −28°C) and palladium (at 18.5°C) must not be attributed to the characteristic chair conformation of the cyclohexane molecule.

Apparent Activation Energy.—Since the deuterium content of hydrogen in the present experiments was only 36.1 atomic %, the apparent activation energy derived from k_D plot is of significance. As seen in Table IV, the agreement between the present value and that obtained by Anderson and Kemball is well maintained. Although the pressure-dependence of this exchange over evaporated tungsten films was not further studied, the kinetic consideration discussed in the preceding paper may equally fit the present results. Hence the apparent activation energy experimentally found (10.3 kcal./mol.) would imply the activation energy of chemisorption of cyclohexane.

Deuterium Isotope Effect.—The deuterium isotope effect for the exchange of cyclohexane on evaporated tungsten films was studied by conducting additional experiments. After the usual determination of the gas phase compositions in equilibrated mixtures, the reaction vessel was rapidly evacuated and the gases newly desorbed from the surface were collected and analysed. Typical results are summarized in Table V. As seen in Table V, at 102°C the present exchange reaction might be influenced to some extent by the deuterium isotope effect. However, the present analytical results on the newly desorbed gases shown in Table V inevitably contain some uncertainties, since only a minute quantity of gases was newly desorbed from the surface. From this fact, it seems rather reasonable, so far as the present experiments were concerned, to consider that the deuterium isotope effect gives no significant influence upon the present exchange reaction.

Summary

Isotopic exchange reaction between cyclohexane and deuterium over evaporated tungsten films has been studied mass-spectrometrically at the temperature range 79~111°C. The present results are summarized as follows;

1) The production of highly deuterated products in the initial stage of this exchange requires a process of multiple exchange.

2) Evaporated tungsten films showed, however, little tendency for multiple exchange, while evaporated molybdenum films promoted multiple exchange to a large extent.

3) One can observe no discontinuities which separate the concentrations of $C_6H_6D_6$ and $C_6H_5D_7$.

4) It seems reasonable to consider that marked discontinuities between $C_6H_6D_6$ and $C_6H_5D_7$ observed by Anderson and Kemball for evaporated films of rhodium and palladium must not be attributed to the characteristic chair conformation of the cyclohexane molecule.

5) The deuterium isotope effect gives no significant influence upon the overall reaction of this exchange.

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[3] R. L. Burwell, Jr., and R. H. Tuxworth, *J. Phys. Chem.*, **60**, 1043 (1956).

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