Isotope Effects in Exchange Reactions of n-Hexane on Palladium Films

E. F. MEYER AND C. KEMBALL

From the Department of Chemistry, The Queen's University of Belfast, Northern Ireland

A series of experiments was carried out to investigate isotope effects in the exchange of n-hexane with deuterium and heavy hexane with hydrogen on palladium films. A kinetic isotope effect is associated with the rate-determining steps of the exchange reaction, which are the initial process of adsorption of the hydrocarbon on the surface and the final desorption of the hydrocarbon from the surface (both processes necessarily occur at the same rate). Thus C_6D_{14} exchanges more slowly than C_6H_{14} and requires an additional activation energy of about 2 kcal/mole.

Regardless of the direction of the exchange, massive amounts of the interconversion of different types of adsorbed species of hydrocarbon occur on the palladium surface before the molecules return to the gas phase. When exchange takes place with mixtures of hydrogen and deuterium there is an equilibrium isotope effect associated with this interconversion process such that the D/H ratio attained by the hydrocarbon is about twice the corresponding D/H ratio in the deuterium-hydrogen mixture. The mean deuterium content of the hexanes at equilibrium shows a similar tendency for the preferential accumulation of deuterium in the "hexane" relative to the "hydrogen." However, there is no appreciable equilibrium isotope effect on the relative amounts of the different isotopic hexanes which may be estimated quite accurately on the assumption that the atoms are randomly distributed between the various isotopic hydrocarbons.

INTRODUCTION

The catalytic exchange of alkanes with deuterium on palladium metal often yields a high percentage of the perdeuteroalkane as an initial product of the reaction (1). The presence of such highly exchanged products after only one effective residence of the hydrocarbon molecule on the surface has been explained on the following assumptions:

(a) The initial step in the chemisorption of the alkane, i.e., the formation of an adsorbed alkyl radical C_nH_{2n+1}, is slow and it follows from the concept of microscopic reversibility that the reverse reaction, the desorption of alkyl radicals yielding alkane molecules as products, is also slow.

(b) The interconversion of different types of adsorbed species is rapid; such species include C_nX_{2n+1} and C_nX_{2n} (X representing H or D) and, in some cases, more highly dissociated entities such as C_nX_{2n-1} and C_nX_{2n-2}.

(c) The replacement of chemisorbed hydrogen atoms by deuterium is extremely fast so that adsorbed hydrocarbon species have little chance of acquiring a hydrogen atom and always gain a deuterium atom on "rehydrogenation" in the early stages of the exchange process.

The object of this work is to find out how much of this high degree of exchange is a genuine characteristic of palladium as a catalyst and how much of it is the result of preferential cleavage of C–H bonds in the adsorbed species. Flanagan and Rabinovitch (2) have shown that C–H bonds break more readily than C–D bonds in adsorption processes and such a kinetic isotope effect would cause a preferential retention of a deuterium atom, once acquired, in adsorbed species undergoing interconversion reactions on the surface.

We selected n-hexane as a suitable hydrocarbon for the investigation of isotope effects. Gault and Kemball (3) examined

the exchange of *n*-hexane with deuterium over palladium films and showed that over 80% of the initial products consisted of the perdeutero compound C_6D_{14} so that any substantial isotope effect should be easily detectable. We planned to carry out three different types of experiment. Firstly, the exchange of pure compounds, i.e., light hexane and deuterium, and heavy hexane and hydrogen, was examined and we label such experiments CH/D and CD/H, respectively. Secondly, we carried out exchange using pure hydrocarbons and mixtures of hydrogen and deuterium—these are designated CH/H + D and CD/H + D. Finally, we followed the exchange of mixed hydrocarbons with a mixture of hydrogen and deuterium, i.e., CH + CD/H + D.

EXPERIMENTAL

The source and preparation of the chemicals, the apparatus, the experimental and analytical procedures were closely similar to those already described (*3*). Heavy hexane, C_6D_{14}, was prepared by repeated exchange of light hexane with deuterium over a tungsten film and the final product contained about 95% C_6D_{14} and 5% C_6HD_{13}. The reaction mixtures which were admitted to the reaction vessel (198 ml) at 0°C are given in Table 1 together with the lowest temperature at which each reaction was studied.

RESULTS AND DISCUSSION

Exchange with Pure Compounds

The initial distributions of the principal products from the CH/D and CD/H ex-

periments are given in Table 2 in which the

TABLE 2
INITIAL DISTRIBUTIONS OF PRODUCTS FROM THE
CH/D AND CD/H EXPERIMENTS

Experiment	x_{13} compound[a] (%)	x_{14} compound[a] (%)	Mean number of x atoms in products[a]
CH/D/1	9	91	13.9
CH/D/2	11	89	13.9
CD/H	17	83	13.8

[a] Ignoring a small amount of x_1 compound formed as a product.

symbol x is used for the atom entering the hydrocarbon. As observed in the earlier work (*3*), a small percentage of $C_6H_{13}D$ was also formed as an initial product in the CH/D experiments but it was not taken into account in the distributions reported in Table 2 because the estimation of the corresponding formation of a small percentage of C_6HD_{13} in the CD/H experiment was inaccurate, owing to the presence of this isotopic species in the reactant used. The initial degree of exchange was only slightly less extensive in the CD/H experiment than in the two CH/D experiments and so it is obvious that despite isotope effects, really massive amounts of interconversion of adsorbed hydrocarbon radicals must occur on the surface of the catalyst.

The initial rate of exchange of light hexane k_H was faster than the corresponding rate for heavy hexane k_D and the ratio k_H/k_D was about 4 at 80°C. This fact provides good evidence in support of the assumption that it is the rate of the initial adsorption/desorption of the hydrocarbon which governs the over-all rate of exchange.

TABLE 1
REACTION MIXTURES AND THE FIRST TEMPERATURE USED

Experiment	Hexane pressure (mm)	Ratio $\frac{\text{"hydrogen"}}{\text{"hexane"}}$	Ratio D/H in "hydrogen"	Initial temp. used for reaction (°C)
CH/D/1	3.6	10.6	200	60°
CH/D/2	3.6	10.1	200	60°
CD/H	3.8	10.4	2×10^{-4}	79°
CH/H + D/1	3.5	9.7	0.99	79°
CH/H + D/2	2.6	15.2	1.00	79°
CD/H + D	3.1	11.1	1.01	79°
CH + CD/H + D	1.4 + 1.7	17.7	1.00	79°

Flanagan and Rabinovitch reported a ratio of 2.6 at 84°C for the relative rates of dissociation of C–H and C–D bonds in the methyl group of adsorbed ethyl radicals on nickel. The difference in the rates of exchange of C_6H_{14} and C_6D_{14} had some important effects on the product distributions at later stages of the reactions, as can be seen from the data in Table 3 where the

TABLE 3

LATER PRODUCT DISTRIBUTIONS IN THE CH/D AND CD/H EXPERIMENTS

Compound	CH/D/1 when M_x = 3.07[a] (%)	CD/H when M_x = 2.93 (%)	Compound	CH/D/1 when M_x = 3.07 (%)	CD/H when M_x = 2.93 (%)
x_0	74.3	70.7	x_8	0.2	0.3
x_1	1.6	4.2[b]	x_9	0.3	1.1
x_2	0.4	—	x_{10}	0.5	2.4
x_3	0.2	0.3	x_{11}	1.0	4.7
x_4	0.1	0.4	x_{12}	2.5	6.5
x_5	0.1	0.4	x_{13}	6.7	5.8
x_6	0.3	0.05	x_{14}	11.7	2.9
x_7	0.1	0.2			

[a] M_x represents the mean number of x atoms in the hexane.

[b] This percentage is high because of the presence of C_6HD_{13} in the initial mixture.

isotopic compositions of the hexanes in the CH/D and CD/H experiments are compared at the point where the mean number of atoms replaced M_x is about 3. In the CH/D experiment the most abundant product at this stage was the x_{14} compound (C_6D_{14}) and as the exchange continued the amount of this isotopic species passed through a maximum at 15% before declining to the final equilibrium percentage. On the other hand, in the CD/H the amount of the x_{14} compound (C_6H_{14}) had passed through a maximum percentage of about 3.5% before the stage shown in Table 3, at which the most abundant product was the x_{12} compound. These differences between the two experiments were caused by the fact that the reverse exchange of the product molecules like C_6H_{14} and $C_6H_{13}D$ was faster in the CD/H experiment than the corresponding reverse exchange of C_6D_{14} in the CH/D experiment. The subsidiary maximum in the product distribution for

the CD/H experiment at the x_4 and x_5 compounds ($C_6H_4D_{10}$ and $C_6H_5D_9$) which is apparent in Table 3 was a further consequence of isotope effects, as will be made clear by the results in the next section.

Exchange with Pure Hexane and Mixtures of Hydrogen and Deuterium

The exchange of light hexane and of heavy hexane with equimolar mixtures of hydrogen and deuterium was examined in order to find out more about the influence of isotope effects on the initial distribution of products and the extent to which the massive amounts of interconversion of adsorbed radicals lead to initial products in equilibrium with the gas-phase hydrogen and deuterium. Since the initial products are formed by the reaction of a very small amount of hydrocarbon with a large excess of "hydrogen," the same product distribution should be found in reactions of both C_6H_{14} and C_6D_{14} with equimolar mixtures of hydrogen and deuterium if complete equilibration was attained by the interconversion reactions on the surface of the catalyst.

There are many examples (1) which indicate that the distribution of deuterium between a "hydrocarbon" and "hydrogen" at equilibrium does not correspond to the expected random or classical distribution but shows a preferential tendency for deuterium to be in the "hydrocarbon" rather than the "hydrogen." In order to understand the results of the CH/H + D and CD/H + D experiments, it is essential to have some quantitative estimate of the equilibrium distribution of deuterium between "hexane" and "hydrogen." We obtained this by allowing complete equilibrium to be attained and using the analysis of the mixture to evaluate the ratio

$$R = \frac{(D/H)_{hex}}{(D/H)_{hyd}} \tag{1}$$

The value of R found at 137°C was 2.18 for a mixture in which the total numbers of hydrogen and deuterium atoms were approximately equal. Some of the data quoted by Gault and Kemball (3) give a value of R of 2.54 at 140°C, but the mixture they

used was rich in deuterium and there may be a slight variation in R with the isotopic composition of the gas.

If $R = 2.18$ we should expect hexane molecules equilibrating with an equimolar mixture of hydrogen and deuterium to acquire an average of 9.6 D atoms and the probable composition of such a mixture is shown in the second column of Table 4.

TABLE 4
INITIAL PRODUCT DISTRIBUTIONS FROM THE CH/H + D AND CD/H + D EXPERIMENTS COMPARED WITH A CALCULATED EQUILIBRIUM DISTRIBUTION

Compound[a]	Calculated (%)	CH/H + D/1 (%)	CH/H + D/2 (%)	CD/H + D (%)
d_2	—	1	1	—
d_3	—	2	3	—
d_4	0.2	2	3	—
d_5	0.9	3	4	—
d_6	3.0	6	5	—
d_7	7.5	7	8	6
d_8	14.2	15	10	9
d_9	20.6	19	15	18
d_{10}	22.4	15	15	29
d_{11}	17.8	15	18	20
d_{12}	9.7	8	10	17
d_{13}	3.2	5	5	1[b]
d_{14}	0.5	2	3	—[c]
Mean deuterium content M_D	9.6	9.1	9.2	10.0

[a] The formation of a small percentage of the d_1 compound is ignored in the CH/H + D experiments.

[b] Subject to substantial error because of the presence of C_6HD_{13} in the initial mixture.

[c] No value can be given because C_6D_{14} formed as a product cannot be distinguished from the reactant C_6D_{14}.

This distribution was obtained by assuming that the equilibrium constants of the interconversion equilibria of the type

$$C_6H_nD_{14-n} + C_6H_{n+2}D_{12-n} = 2C_6H_{n+1}D_{13-n} \quad (2)$$
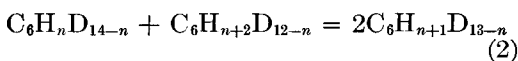
may be adequately represented by classical theory and evaluated on the assumption of a random distribution of atoms between the isotopic hexanes (1). Evidence in support of this assumption will be given in a later section. The remaining columns of Table 4 give the experimental initial product distributions from the CH/H + D and the CD/H + D experiments. As these involved the measurement of small amounts of a number of products they could not be obtained with great accuracy, but the results for CH/H + D/1 and CH/H + D/2 show satisfactory reproducibility. Both types of experiments gave distributions which showed some similarity with the equilibrium distribution, but it is obvious that mechanistic considerations play some part in determining the products formed in the initial reaction. The main type of isotope effect is an equilibrium effect in that the values of M_D in the products from C_6H_{14} were about 0.4 below the expected value of 9.6, whereas the value of M_D from C_6D_{14} exceeded 9.6 by the same amount. Thus, both types of experiments led to product distributions with a broad maximum centered around d_9, d_{10}, and d_{11}, and not around d_7. The position of the subsidiary maximum already noted in the results for the CD/H experiment in Table 3 is clearly similar to the maximum in Table 4 and due to the same effects. Gault and Kemball (3) pointed out that although very extensive exchange occurs with hexane on palladium in the initial reaction, the products formed differ significantly from an equilibrium distribution and our results are in excellent agreement with this conclusion.

Rates and Exchange of Mixed Hexanes

Data for the initial rates of disappearance of the reactant hydrocarbon (k_H or k_D expressed as %/min for 100 cm² of apparent surface area of the films) at various temperatures are given as Arrhenius plots in Fig. 1. The values of k_H determined in this work agree satisfactorily with those obtained earlier (3). The activation energies associated with k_H and k_D are 19.4 and 21.6 kcal/mole, respectively, but both are subject to experimental error and so little significance should be attached to the actual value of 2.2 kcal/mole for the ΔE associated with the isotope effect.

As there was some variation in the catalytic activity of different palladium films we carried out the simultaneous exchange
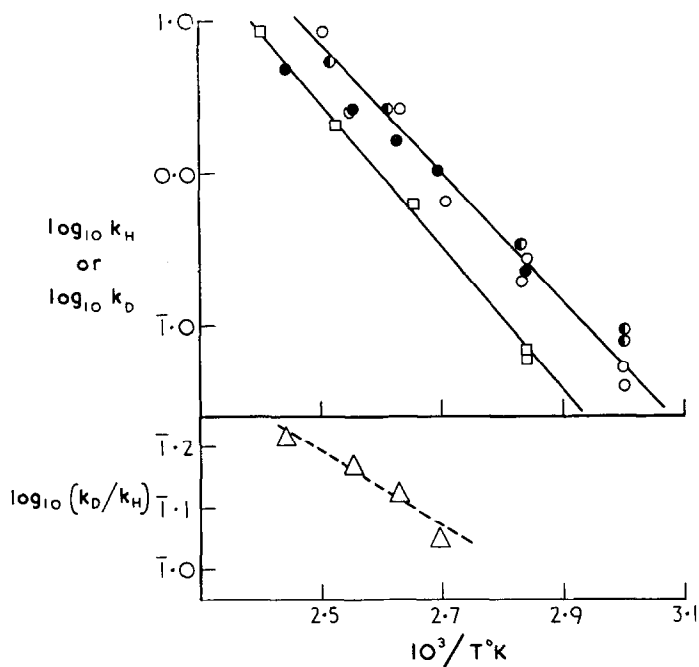
FIG. 1. Arrhenius plots for the rates of exchange: circles represent values of the initial rate of exchange of C_6H_{14}, k_H, expressed as %/min 100 cm² of apparent surface; half-filled circles are data from Gault and Kemball (3), and filled circles from the CH + CD/H + D experiment; squares represent values of the initial rate of exchange of C_6D_{14}, k_D; triangles are the ratios of k_D/k_H in the CH + CD/H + D experiment.

TABLE 5

PRODUCT DISTRIBUTIONS AT VARIOUS STAGES IN THE CH + CD/H + D EXPERIMENT AND MEAN DEUTERIUM CONTENTS

Compound	Observed distributions						Calculated distribution[a]
d_0	38.1	24.9	11.7	4.4	0.1	—	—
d_1	0.4	0.5	0.4	0.2	—	—	—
d_2	—	0.3	0.3	0.2	0.1	0.1	—
d_3	—	0.3	0.3	0.3	0.3	0.3	0.3
d_4	—	0.3	0.6	0.8	1.0	1.1	1.1
d_5	0.3	0.7	1.5	2.0	3.0	3.5	3.5
d_6	0.5	1.5	3.1	4.4	6.8	8.1	8.2
d_7	0.8	2.8	5.5	7.9	11.9	14.6	14.7
d_8	1.4	4.2	7.9	10.9	16.3	20.2	20.3
d_9	1.9	5.0	8.9	11.8	17.2	21.1	21.1
d_{10}	2.0	4.7	7.7	9.8	13.4	16.6	16.6
d_{11}	1.3	3.1	4.9	6.0	7.9	9.5	9.5
d_{12}	0.8	1.7	2.5	3.0	3.6	3.9	3.7
d_{13}	2.9	3.1	3.2	3.2	2.7	1.0	0.9
d_{14}	49.6	46.9	41.5	35.1	15.7	—	0.1
M_D	8.14	9.12	9.96	10.22	9.48	8.56	8.56

[a] Calculated with classical values of the interconversion equilibria (2) and $M_D = 8.56$.

of light and heavy hexane with an equi-
molar mixture of hydrogen and deuterium
in order to obtain a direct comparison of
the rates of exchange of the two forms of
hexane. Rates of reaction in this CH +
CD/H + D experiment were determined at
79°, 98°, 107.3°, 118.7°, and 136°C and the
values of k_H are shown as filled circles in
Fig. 1. The rates at the lower temperatures
agreed with the values of k_H in other ex-
periments but those at the two highest
temperatures indicate some decline in the
activity of the film, presumably due to the
self-poisoning of the reaction by the forma-
tion of strongly adsorbed species on the
palladium surface—a topic which has been
discussed by Gault and Kemball (3). The
ratio of k_D/k_H increased from 0.111 at 98°C
to 0.164 at 136°C and the Arrhenius plot
for the ratio shown in Fig. 1 gave an ap-
proximate value of 2.7 kcal/mole for ΔE.

Some product distributions at various
stages throughout the CH + CD/H + D
experiment are given in Table 5 because
they confirm a number of features shown
in the other runs. In the early stages the
products show a broad maximum centered
around the d_9 and d_{10} compounds and this
maximum gradually moves to the equilib-
rium position centered around the d_8 and
d_9 compounds. The more rapid exchange of
C_6H_{14} compared with C_6D_{14} is shown very
clearly by the results in Table 5. This dif-
ference in the rate of reaction of the two
isotopic forms of the hexane causes the
mean deuterium content M_D of the hexanes
to pass through a maximum during the
course of the experiment. The subsequent
decline of M_D to the equilibrium value is
associated with the disappearance of the
slowly reacting C_6D_{14} compound. The last
experimental distribution given in Table 5,
which was obtained at 208°C, represents
equilibrium and agrees very closely with a
calculated distribution for the same value
of M_D. This agreement confirms that the
interconversion equilibria between isotopic
hexanes (2) can be obtained quite accu-
rately on classical theory.

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