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Hydrogenation of Propene on Pt Catalyst in Aqueous Solution

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Hydrogenation of propene on Pt catalyst was studied in 0.5 *M* D_2SO_4. The distribution of deuterium in the product propane consists of two segments *A* and *B* where maxima appear at d_2- and d_8-species, respectively. Precise analyses of the mass and NMR spectra of the propane clarified the positions of the deuterium atoms in the molecule; (i) both the methylenic hydrogens are deuterium for $d_3 \sim d_6$ species in segment *A*, (ii) the deuterium atoms are omnipresent in one of the two methyl groups for 40% of $d_4 \sim d_6$-species in segment *A* and are distributed in both methyl groups for the rest, and (iii) deuterium atoms in segment *B* are randomly distributed in the eight hydrogen atoms. The above result (i) indicates the preferential formation of *n*-propyl rather than iso-propyl as a reaction intermediate, and (ii) and (iii) point to the presence of different, restricted or free rotational states for the isopropyl intermediate around the C-metal bond. The H/D exchange in the free rotational intermediate is extremely fast in segment *B* and relatively slow in segment *A*.

INTRODUCTION

Hydrogenation of lower olefins on metal catalysts has been widely studied in the gas phase. The associative mechanism in which adsorbed olefin molecule accepts a hydrogen atom to form an adsorbed alkyl radical (half-hydrogenated state) and then a second hydrogen atom to form paraffin, has generally been accepted from the 1960's (*1*). In addition, Bond *et al.* (*2*) have shown that the alkyl radical undergoes the H/D exchange reaction with olefin and the disproportionation reaction forming olefin and paraffin. A dissociative species of olefin was also reported to participate in the exchange reaction of olefin with D_2 (*3, 4*). These studies are based on the analyses of mass spectra of paraffin and/or microwave spectra of deuterium-exchanged olefin. However, the number of deuterium atoms taken up into the paraffin is rather limited in the deuteration of olefin in the gas phase, because the fraction of deuterium in adsorbed hydrogen atoms, f_D, is rather low, for example, 0.72–0.76 for the hydrogenation of 1,3-butadiene (*5*) and 0.33–0.50 for that of ethylene (*2*) on Pt/Al_2O_3. The lower f_D is due to both the slow rate of the exchange reaction of the adsorbed hydrogen with D_2 and the small deuterium capacity of D_2 in the gas phase. Phillipson and Burwell (*6*) used deuterium-containing organic solvents such as CH_3COOD, CH_3OD, $(CH_3)_3COD$, THF (tetrahydrofuran)-D_2O, and $D_2NCH_2CH_2OD$—CH_3OD for the hydrogenation of olefins such as cyclopentene, cyclohexene, and 1-hexene on Pt/Al_2O_3, and were successful in raising f_D to 0.82–0.90. In such a system, the exchange reaction, $H(a) + ROD \rightleftarrows D(a) + ROH$, proceeds rather rapidly. On the other hand, we have carried out the deuteration in 0.5 *M* D_2SO_4–D_2O solution and found out that f_D is always kept above 0.9 during the reaction (*7*) through the fast equilibrium step of D^+-discharge. Therefore, the study in an aqueous system is expected to provide enhanced H/D exchange and hence useful information in elucidating a rather complicated reaction mechanism on metal catalysts. We have already reported the new information (*8*) that two maxima appear in each distribution of deuterium in paraffins produced from propene, 2-methylpropene and 1-butene on Pt; one maximum is at partially deuterium-exchanged paraffin, often at d_2-species ($C_nH_{2n}D_2$, $n = 3, 4$), and the

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other at or near perdeuteroparaffin It has been concluded that the partially deuterium-exchanged paraffin is produced through the H/D exchange of only the vinylic hydrogens via the first, reversible addition of a hydrogen atom The present work aims to reconfirm the above conclusion by determining the positions of deuterium atoms in methyl and methylene groups of propane Thus, special attention is paid to the precise analyses of the mass and NMR spectra On the basis of the distribution thus obtained, the reaction mechanism is discussed in detail

EXPERIMENTAL

A catalyst of Pt net (4 *N* purity, apparent area 80 cm^2) was immersed in 0 5 *M* D_2SO_4 solution prepared from D_2SO_4 (Merck, 99% D) and D_2O (Merck, 99 75% D), and was subjected to an electrochemical pretreatment, i e , anodic oxidation at 1 8 V vs rhe (reversible hydrogen electrode) for 5 min and then reduction at 0 V for 5 min just before the reaction The reaction gas was an atmospheric pressure mixture of propene, D_2 (Showa Denko, Japan, 7 *N* purity) and He (7 *N* purity) The reaction was carried out on open circuit at room temperature in a closed-circulation system

In order to estimate the accurate distribution of deuterium from an observed mass spectrum, the pattern coefficients for each deuteropropane isomer were carefully determined by taking into account the two factors which have a great influence on the results, one is the ratio of the cleavage of C—H to C—D (isotopic effect) and the other is the ratio of the cleavage of C—H in CH_3— to that in —CH_2— groups (positional effect) The former is estimated as 1 5 from the mass spectra of CD_3 CD_2 CD_3 and CH_3 CH_2 CH_3, and the latter as about 0 from the mass spectra of CD_3 CH_2 CH_3 and CH_3 CH_2 CH_3, respectively These values indicate that C—H bond cleaves 1 5 times more easily than C—D bond does and that the cleavage occurs exclusively in the methylene group The distribution thus calculated is much more reliable than the previous one (*8*) where the above two effects were not taken into account However, it will be noticed that the other distribution, calculated under the assumption of zero positional effect, for 2-methylpropane produced from 2-methylpropene on Pt/graphite in 0 5 *M* D_2SO_4 (*8*) remains valid since the *tert*-alkyl cation is very stable compared with the *sec*-alkyl cation and is formed so easily that the difference between the C—H and C—D cleavage in the methine group cannot be detected, as confirmed by the mass spectra of CD_3 CD $(CD_3)_2$ and CH_3 CH $(CH_3)_2$

The NMR spectrum of propane, dissolved in $CDCl_3$ and sealed into a glass tube, was measured by a high-resolution NMR spectrometer (400 MHz, JEOL, JNM-FX-400), in order to estimate the respective average numbers of deuterium taken up in CH_3— and —CH_2—

RESULTS AND DISCUSSION

1 Distribution of Deuterium in Deuteropropane

We first describe the distribution of deuterium in deuteropropane estimated from mass spectra with the pattern coefficients mentioned above As an initial stage we assume that one deuterium is always taken up in the methylene group of $d_2 \sim d_8$-species since the double bond is deuterated under conditions with a high-deuterium fraction in adsorbed hydrogen atoms The distribution thus obtained (Fig 1 (○)) is clearly composed of two segments, *A* and *B*, *A* consists of less-deuterated species where a maximum appears at $d_2 \sim d_3$-species and *B* consists of highly deuterated species where a maximum appears at perdeuteropropane The present fraction for d_6-species amounts to ca 10%, in contrast to the previous value of ~0% (*8*), as a result of the due consideration of the isotopic and positional effects

Such a two-maximum distribution of deuterium has not been reported in gaseous heterogeneous hydrogenation nor even in

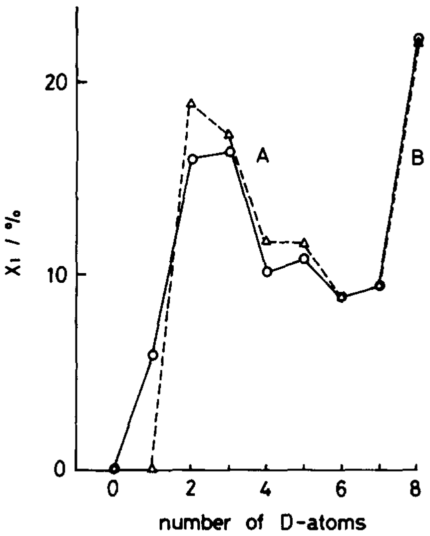


FIG 1 Distribution of deuterium in propane produced by the deuteration of propene on Pt net in 0 5 *M* D_2SO_4 In the calculation of these distribution from mass spectrum, one (○) or two (△) methylenic hydrogens are assumed to be always deuterium

the hydrogenation in deuterium-containing organic solvents (*6*) In the latter case of the hydrogenation of cyclopentene, however, it should be mentioned that their *N*-profiles deduced from the monotonous distributions of deuterium clearly reveal two maxima, one at N_2 and the other at N_5 (N_i, the fraction of the molecules in which *i* hydrogen positions have been equilibrated with the surface H/D pool) The maximum at N_2 is easily understood in terms of the simple addition of two hydrogen atoms to the double bond The other maximum at N_5 suggests the presence of multiexchange giving rise to per-exchanged species to a considerable extent under the conditions that one and the same side of cyclopentane keeps an interaction with the catalyst surface Such a double-maximum distribution clearly develops in the distributions of deuterium in our experiments In the present system (0 5 *M* D_2SO_4), f_D is much higher (close to unity) and hence the observed distribution of deuterium directly approximates its *N*-profile

II Positions of Deuterium Atoms in Deuteropropane

Next, we will determine positions of the deuterium atoms taken up in deuteropropane by using the distribution of Fig 1 and NMR spectra NMR spectra show that 3 12 deuterium atoms go into methyl groups and 1 67 into the methylene group, respectively (Table 1, I-(1)) In the following it is shown how these numbers are obtained from the distribution of Fig 1 using the model described below

Segment B We first assume that segment *B* represents the random distribution of deuterium in the eight hydrogen atoms because of a high production of perdeuterospecies (d_8-) which are produced only by

TABLE 1

(DN)'s in Methyl and Methylene Groups of the Deuteropropane

	I[a]			II[a]		
	CH_3— —CH_3	—CH_2—	Total	CH_3— —CH_3	—CH_2—	Total
(1) $(DN)_{obs}$	3 12	1 67	4 79	3 22	1 68	4 90
(2) $(DN)_B$	1 91	0 64	2 55	1 90	0 63	2 53
(3) $(DN)_{A\,d}$	0 60	0 60	1 20	0 63	0 63	1 26
(4) $(DN)_{A\,ex}$	0 60	0 44	1 04	0 64	0 48	1 12
(1) − {(2) + (3) + (4)}	0 01	−0 01		0 05	−0 06	

[a] I and II are based on the distributions of deuterium shown in Fig 1 by circle and triangle, respectively

the extremely fast H/D exchange over all the hydrogen atoms of the molecule. Thus, the fractions of d_8- and d_7-species can give the deuterium fraction in adsorbed hydrogen atoms, f_D, and then the expected contribution at each less-deuterated species by using a binomial formula based on the random distribution. Calculation shows that $f_D = 0.95$ and that the contribution sharply drops from 19.1% at d_6 to 1.8% at d_5 and becomes negligible at $d_4 \sim d_0$. By summing up the contributions at each d_i, we can estimate the relative proportion of segment B and hence of A as

$$\sum_{i=5}^{8} X_i^B = 0.35, \qquad \sum_{i=0}^{6} X_i^A = 0.65,$$

where X_i^B and X_i^A are the fraction of d_i-species in segments B and A, respectively, and $X_i^B + X_i^A$ gives the observed fraction of d_i-species. Here, X_7^A and X_8^A are zero. The random distribution (segment B) also gives a contribution to the average number of deuterium in methyl and methylene groups, denoted as $(\mathrm{DN})_B^{\mathrm{CH_3}}$ and $(\mathrm{DN})_B^{\mathrm{CH_2}}$, by a proportional allotment as

$$(\mathrm{DN})_B^{\mathrm{CH_3}} = \frac{6}{8} \sum_{i=5}^{8} X_i^B \tag{1}$$

and

$$(\mathrm{DN})_B^{\mathrm{CH_2}} = \frac{2}{8} \sum_{i=5}^{8} X_i^B \tag{2}$$

The respective contributions are listed in Table 1, I-(2).

Number of deuterium atoms taken up by the deuteration (*Segment* A). Next, we examine segment A. At first, the number of deuterium atoms which go into the two methyl and one methylene groups by the deuteration without H/D exchange is estimated. Obviously, the deuteration introduces 0.95 deuterium atom ($f_D = 0.95$) into both the groups of each deutero-species except d_1. In the latter case, we assume that a deuterium atom has the equal chance to go into the both groups. Thus, the number of deuterium taken up in the methyl group by the deuteration $(\mathrm{DN})_{A,d}^{\mathrm{CH_3}}$ and that in methylene $(\mathrm{DN})_{A,d}^{\mathrm{CH_2}}$, are given by

$$(\mathrm{DN})_{A,d}^{\mathrm{CH_3}} = (\mathrm{DN})_{A,d}^{\mathrm{CH_2}} = 0.48\, X_1^A + 0.95 \sum_{i=2}^{6} X_i^A \tag{3}$$

Number of deuterium atoms taken up by the H/D exchange (*Segment* A). Second, the numbers of deuterium atoms which go into the two methyl and one methylene groups by the H/D exchange, $(\mathrm{DN})_{A,\mathrm{ex}}^{\mathrm{CH_3}}$ and $(\mathrm{DN})_{A,\mathrm{ex}}^{\mathrm{CH_2}}$, are estimated as follows. Subtraction of $(\mathrm{DN})_{A,\mathrm{d}}^{\mathrm{CH_3}} + (\mathrm{DN})_{A,\mathrm{d}}^{\mathrm{CH_2}}$ from the total number of $\sum_{i=1}^{6} i\, X_i^A$ gives the total number of the deuterium atoms introduced by the exchange. Now, a question arises as to the ease of the exchange in the methylene and two methyl groups. We first assume that the original hydrogen atom at the methylene group is in equilibrium with respect to the H/D exchange because of the extremely easy cleavage of the methylene C—H bond. Then, we will show that the DN calculated under this assumption can reproduce the $(\mathrm{DN})_{\mathrm{obs}}$ from the NMR spectrum. Species d_3, d_4, d_5, and d_6 will contain two deuterium atoms in the methylene group from the above assumption and one deuterium atom due to the deuteration in one of the two methyl groups. Thus, the subtraction of these deuterium atoms by taking into account f_D (= 0.95), gives the DN brought by the exchange in the two methyl groups,

$$(\mathrm{DN})_{A,\mathrm{ex}}^{\mathrm{CH_3}} = \sum_{i=3}^{6} (i - 3 \times 0.95) X_i^A \tag{4}$$

Similarly, the DN in the methylene group due to the exchange is calculated as $0.95 \sum_{i=3}^{6} X_i^A$. In addition, a contribution, though it is minor, from d_1 and d_2 species must be taken into account to fulfill the mass balance condition. These species contain 0.95 and 1.9 deuterium atoms due to the deuteration, and the remainder of 1 and 2, i.e., 0.05 and 0.1 are due to the H/D exchange

The latter fractions are added to the above DN since the exchange proceeds much more rapidly in the methylene group than in the methyl groups Thus, we have

$$(\mathrm{DN})_{A\,\mathrm{ex}}^{\mathrm{CH}_2} = 0\ 05\ X_1^A + 0\ 10\ X_2^A + 0\ 95 \sum_{i=3}^{6} X_i^A \quad (5)$$

Calculated values of all the (DN)'s are summarized in Table 1 The subtraction of the (DN)'s from the observed average number of deuterium, $(\mathrm{DN})_{\mathrm{obs}}$, results in almost zero in the methyl and methylene groups From these results, we can conclude that both hydrogens attached to the methylenic carbon are deuterium for $d_3 \sim d_6$-species

Recalculation of the distribution of deuterium Now, the above conclusion requires recalculation of the distribution of deuterium by taking into account that both the hydrogens in the methylene group are deuterium in $d_3 \sim d_6$-species in segment *A* The final distribution is shown in Fig 1 (△) The same procedure for the estimation of the above (DN)'s is repeated New (DN)'s are summarized in Table 1, II No essential difference is observed

Throughout the above calculation, we have assumed that f_D is uniform over the surface, in contrast to the conclusion by Phillipson and Burwell (*6*) that there are at least two sets of surface sites different in f_D, on larger f_D sites most of the hydrogenation accompanied with multiple H/D exchange takes place, and on smaller f_D sites mainly simple addition hydrogenation occurs This model will be disproved as follows

Since the present value of $f_D = 0\ 95$ is derived from X_7 and X_8, the fractions of the multi-exchanged propanes, the other f_D must be estimated from the fractions of the species formed by the simple addition X_0 and X_1 are, however, almost zero in the distribution (Fig 1) Thus, the f_D must be close to unity (if f_D is low, a significant amount of X_0 and X_1 must be observed) Thus, we regard f_D as uniform, as a first approximation

Partition of deuterium between two methyl groups (*Segment* A) The last question to be solved is whether the deuterium atoms in the two methyl groups are localized in one methyl group or spread over the two methyl groups The localized and delocalized structures for $d_4 \sim d_6$-propane in segment *A* are

	localized structure	delocalized structure
d_4	$CHD_2—CD_2—CH_3$ (0 4)	$CH_2D—CD_2—CH_2D$ (0 6)
d_5	$CD_3—CD_2—CH_3$ (0 1)	$CHD_2—CD_2—CH_2D$ (0 9)
d_6	$CD_3—CD_2—CH_2D$ (0 4)	$CHD_2—CD_2—CHD_2$ (0 6)

The figures in parentheses show the probability of appearance of each species when the deuterium atoms enter randomly into the two methyl groups This random distribution is named "model I" in contrast with that giving only the species of localized structure called "model II " These two models are now examined to see which one reproduces the observed relative intensity (Table 2) of the peak at *m*/*e* = 34 ($CD_3—CD_2^+$) to that at *m*/*e* = 33 ($CHD_2—CD_2^+$ or $CD_3—CHD^+$) Only the foregoing three fragments give peaks which are free from any fragments formed by the cleavage of a carbon–hydrogen bond of

TABLE 2

Relative Intensity of the Peak at *m*/*e* = 34 to That at *m*/*e* = 33

Run	Observed	Calculated		Contribution of Model II (%)
		Model I	Model II	
1	1 90	1 5	2 7	33
2	1 92	1 6	2 3	44
3	1 94	1 5	2 6	38

heavier C_2-species and free from the effect of a background of O_2 at $m/e = 32$ The relative intensity of the peak at $m/e = 34$ to that at $m/e = 33$, R, is estimated from the distribution of deuterium in propane (Fig 1) by

$$R = \frac{0\ 05X_5^A + 0\ 20X_6^A + 0\ 02X_5^B + 0\ 105X_6^B + 0\ 375X_7^B + X_8^B}{0\ 2X_4^A + 0\ 45X_5^A + 0\ 60X_6^A + 0\ 265X_5^B + 0\ 535X_6^B + 0\ 625X_7^B} \qquad (6)$$

for model I and

$$R = \frac{0\ 5X_5^A + 0\ 5X_6^A + 0\ 02X_5^B + 0\ 105X_6^B + 0\ 375X_7^B + X_8^B}{0\ 5X_4^A + 0\ 265X_5^B + 0\ 535X_6^B + 0\ 625X_7^B} \qquad (7)$$

for model II, where each coefficient is determined as illustrated in Table 3 The calculated R's for three separate runs are summarized in Table 2 and show about 40% occurrence of model II and about 60% model I

III Deuteration of 2-Methylpropene

In the deuteration of 2-methylpropene on Pt/graphite, however, species of the localized structure become main products Figure 2 shows the distribution of deuterium in 2-methylpropane where two segments A and B separate clearly Since the fraction of d_5 is definitely zero and the maximum number of deuterium in segment A is four, it is concluded that the deuterium atoms in segment A are localized as exemplified below for d_4-species

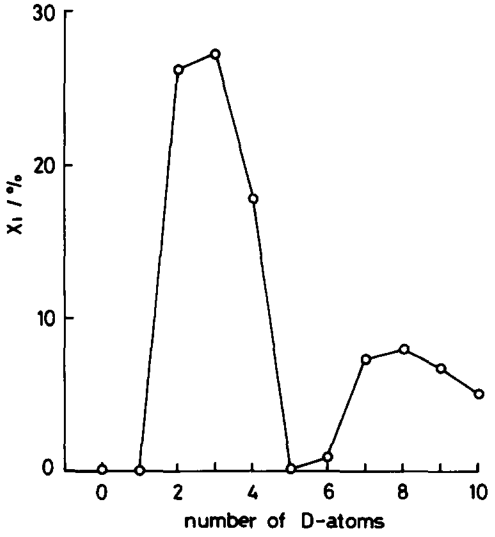
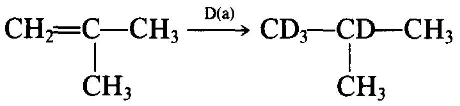


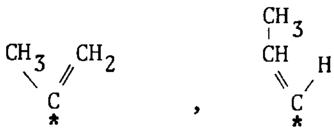
Fig 2 Distribution of deuterium in 2-methylpropane formed by the deuteration of 2-methylpropene on Pt/graphite in 0 5 M D_2SO_4



$$\underset{\displaystyle CH_3}{CH_2{=}\overset{}{C}}{-}CH_3 \xrightarrow{D(a)} CD_3{-}\underset{\displaystyle CH_3}{CD}{-}CH_3$$

IV Reaction Mechanism

The localized distribution of deuterium atoms provides a key for the elucidation of the reaction mechanism for segment A, although for propane it occupies only 40% of segment A These species are formed through the exchange reaction of the vinylic hydrogens of the reactant Dissociatively adsorbed vinyl species such as



were often reported in the literature as the intermediates for the exchange reaction of olefin with D_2 on metal catalysts in the gas phase Such species were first proposed by Farkas *et al* (*3*) for the exchange reaction of ethylene with D_2 on Ni and platinized Pt Hirota and Hironaka (*4*) and Ledoux *et al* (*9*) also suggested the above vinyl species from the microwave spectroscopic data for propene subjected to the exchange reaction on Pt catalyst and for butenes on Pd film However, the exchange through the disso-

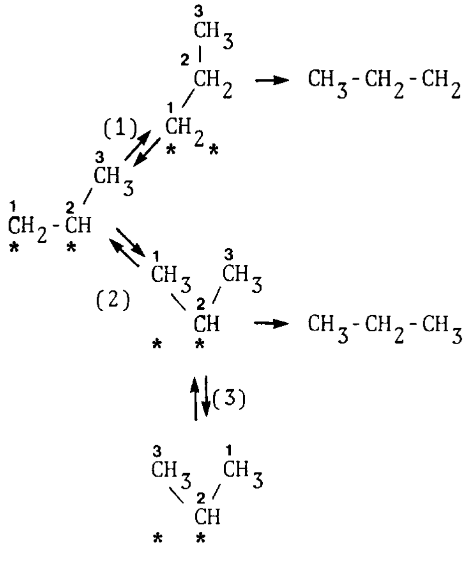
TABLE 3

Coefficients in Eqs (5) and (6)

Segment		Species	Weight	Relative contribution to	
				$m/e = 34$	$m/e = 33$
		Model I			
A	d_4	$CHD_2-CD_2-CH_3$	0.4	0	0.2
		$CH_2D-CD_2-CH_2D$	0.6	0	0
	d_5	$CD_3-CD_2-CH_3$	0.1	0.05	0
		$CHD_2-CD_2-CH_2D$	0.9	0	0.45
	d_6	$CD_3-CD_2-CH_2D$	0.4	0.2	0
		$CHD_2-CD_2-CHD_2$	0.6	0	0.6
		Model II			
	d_4	$CHD_2-CD_2-CH_3$	1	0	0.5
	d_5	$CD_3-CD_2-CH_3$	1	0.5	0
	d_6	$CD_3-CD_2-CH_2D$	1	0.5	0
B	d_5	$CD_3-CD_2-CH_3$	0.04	0.02	0
		$CD_3-CHD-CH_2D$	0.21	0	0.105
		$CHD_2-CD_2-CH_2D$	0.32	0	0.16
		$CHD_2-CHD-CHD_2$	0.32	0	0
		$CD_3-CH_2-CHD_2$	0.11	0	0
	d_6	$CD_3-CD_2-CH_2D$	0.21	0.105	0
		$CD_3-CHD-CHD_2$	0.43	0	0.215
		$CHD_2-CD_2-CHD_2$	0.32	0	0.32
		$CD_3-CH_2-CD_3$	0.04	0	0
	d_7	$CHD_2-CD_2-CD_3$	0.75	0.375	0.375
		$CD_3-CHD-CD_3$	0.25	0	0.25
	d_8	$CD_3-CD_2-CD_3$	1	1	0

ciative intermediate will not be plausible in the present system for the following reasons (i) Propene left unreacted does not contain any deuterium atoms after the reaction This disproves the existence of the dissociative adsorption proposed in the gas phase (ii) Neither the exchange reaction nor hydrogenation proceeds when a mixture of $CH_2{=}CH_2$ and $CD_2{=}CD_2$ is kept in contact with Pt net in aqueous solution (*10*)

The localized distribution of deuterium also cannot be explained by the simple associative mechanism, which allows the release of a hydrogen atom from the two neighboring methyl groups of isopropyl intermediate with the same probability However, if one of the two methyl groups is not allowed to join the exchange reaction, the localized distribution is easily explained by steps (1) and (2) in the following Scheme



Scheme I

An adsorbed propene is half-hydrogenated to either *n*-propyl by step (1) or isopropyl by step (2) The reverse of steps (1) and (2) introduces deuterium into the vinylic position of the reactant In this explanation, it is tacitly assumed that the geometrical orientation of the two carbon atoms, $\overset{1}{C}$ and $\overset{2}{C}$, toward the two adsorption sites is fixed When the rotation of isopropyl intermediate is allowed as shown by step (3), deuterium atoms can enter into both the methyl groups, giving the species of delocalized structure (model I) The clear separation between segment *A* and *B* in the hydrogenation of 2-methylpropane is explained by a complete restriction on the rotation of *tert*-alkyl intermediate because of its bulky structure

The high concentration of deuterium in the methylene of deuteropropane shows the preferential occurrence of step (1) to step (2) This is in accord with the observation in the gas phase by ir spectroscopy that only *n*-butyl is detected in the hydrogenation of the adsorbed 1-butene on Pt/SiO_2 (*11*)

Random distribution of deuterium for segment *B* assumes an extremely fast H/D exchange reaction A free rotational *iso*-alkyl is one of the possible intermediates for this exchange reaction We assumed the same intermediate in the explanation of segment *A*, but this intermediate should be accompanied by an exchange rate much slower than that of the former intermediate

The detailed and accurate analysis of the mass and NMR spectra in the present study reveals (i) the formation of paraffins with the H/D exchange only at the vinylic positions, this exchange produces 40 and 100% of segment *A* at propane and 2-methylpropane, respectively, (ii) the presence of the iso-alkyl with a restricted rotation as the intermediate for the formation of the species mentioned in (i), and (iii) the presence of two kinds of free rotational *iso*-alkyls one gives segment *B* and the other gives 60% of segment *A* for propane The present modified associative mechanism (Scheme 1) will be applicable to the hydrogenation of other olefins The mechanism proposed by Bond *et al* (*2*) is rather complicated and no evidence seems to have been given for the disproportionation of alkyls to form olefin and paraffin

It should be emphasized that the high-deuterium fraction in the surface H/D pool is important in clarification of the reaction mechanism

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