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On the Hyperfine Deuterium Distribution of the Catalytic Reaction of Propene with Deuterium on Copper Powders

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The hydrogenation mechanism of propene on a copper catalyst was investigated at room temperature, using deuterium as the reactant instead of protium. Thereby, not only distributions of the produced deuteropropenes and deuteropropanes were determined by mass spectrometry, but also distributions of the deuterated positions in both monodeuteropropenes and monodeuteropropanes were determined, respectively, by microwave spectrometry and NMR spectrometry. From these two distributions, an extended associative mechanism could be confirmed by assuming half-hydrogenated intermediates of the types $CH_3\text{-}CH_2\text{-}\underset{*}{C}H_2$ and $CH_3\text{-}\underset{*}{C}H\text{-}CH_3$, even though the deuterium-exchange reaction occurs much more frequently via the former species. Double-bond migration was confirmed during the reaction, as has already been proposed on nickel catalyst. Some caution is pointed out on the use of the random-distribution law in discussing the reaction mechanism on the basis of deuterium distribution.

INTRODUCTION

Even though the most advanced methods of research have been applied, studies of the hydrogenation mechanism of olefins on metal catalysts have not reached any final conclusion yet, but rather have become more complicated in some cases (*1*). Tracer studies in which deuterium is used instead of protium and the distribution of the deuterated products of olefins is investigated are an example of such advanced methods. The distribution itself gives interesting knowledge on the hydrogenation mechanism that no other method can do.

Such being the situation, it would be interesting to investigate the catalytic hydrogenation of propene with deuterium in more detail than has hitherto been done, by quantitatively determining the deuterated positions of the exchanged propene and the produced propane. Deuterium distribution of this type will be called "hyperfine distribution" (hfd)† hereafter, in order to discriminate it from the usual deuterium distribution or "fine distribution," which gives us only knowledge on the number of deuterium atoms in some compounds.

It was felt that this new method of research on the hfd of deuterated products would give us exact knowledge on the chemisorbed state of the reactants, as shown already (*2*), and hence might contribute much to the consideration of the hydrogenation mechanism. This expectation was answered in the affirmative in the present research, in which copper was used as the catalyst, in succession to the nickel, palladium, and platinum studied already (*3*). Because dissociation of propene on this metal is difficult, the discussion of the results becomes simplified.

In the section of the discussion, the hydrogenation of propene, which was selected as the next more complex olefin to ethylene, will be found to bear an intimate relation to the double-bond migration, which cannot be known at all by the study of ethylene.

EXPERIMENTAL

Materials. (a) Copper catalyst was prepared by the Sabatier method (*4*), i.e.,

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† This technical term has already been used by one of the present authors (*2*).

black cupric oxide, precipitated by addition of alkaline solution to aqueous copper nitrate, was reduced with hydrogen at 180–190°C. The reduction was continued in a tube to be used as the reaction vessel until no decrease of hydrogen pressure could be measured. It took about 2 weeks. The activity of the catalyst thus prepared was found to be reproducible for propene hydrogenation. The amount of initial cupric oxide was equivalent to 10 g of metallic copper.

(b) Propene of 99.9% purity (Takachiho Trading Co., Tokyo) was purified by bulb-to-bulb distillation, using liquid nitrogen and solid carbon dioxide as refrigerants. No impurities were detected in it by both gas chromatographic and mass spectrometric analysis.

(c) Hydrogen was purified by passing it over silica gel, hot copper wire at 300°C, and through a liquid nitrogen trap, successively.

(d) Deuterium of 99.5% purity (Takachiho Trading Co., Tokyo) was used without purification.

Apparatus and procedure. Since the aim of this study was to obtain qualitative conclusions, a simple static method was adopted to the reaction. The reaction vessel was 200 ml in volume, and it was connected to a conventional vacuum system and gas reservoirs.

Before each experiment, the catalyst was treated with 200 mm of protium at 180–190°C for 24 hr, in order to remove the deuterium which remained in the catalyst. Then, the catalyst was degassed for 3 hr at the same temperature, and cooled down to the reaction temperature (25°C), if not described otherwise.

The reaction mixture, which consisted of $P_{D_2} = 50$ mm and $P_{C_3H_6} = 100$ mm, if not described otherwise, was introduced into the reaction vessel kept at the reaction temperature. Then, pressure change during the reaction was measured by use of a mercury manometer. When the scheduled conversion was reached, hydrocarbons in the product were drawn out from the vessel by condensing them in a tube kept in a liquid nitrogen trap.

In order to subject the hydrocarbons to mass spectrometric analysis, propane was separated from propene with a gas chromatograph which employed a 1-m column of silica gel kept at 80°C.

Analysis. Distributions of deuteropropenes and deuteropropanes were analyzed with a mass spectrometer (Hitachi RMU-5B), installed at the Institute for Protein Research, Osaka University. In the case of propenes, the analysis was carried out in the presence of propanes, but the energy of the ionizing electrons was lowered sufficiently so as to produce only the parent ion of propene. The distribution of the deuteropropanes was also determined mass spectrometrically on the samples mentioned above. In the analysis, it was assumed that all the protium and deuterium atoms in a molecule had equal chances of bond scission in the fragmentation process, because fragment ions produced by loss of one or two protium or deuterium atoms always appeared at such an ionizing voltage that quantitative analysis was possible.

Hyperfine distributions of C_3H_5D or propene-d_1 could be measured by microwave spectrometry in the presence of C_3H_6 or propene-d_0 and highly deuterated propenes, so that four subspecies of propene-d_1* could be determined, as done in the previous reports (*3*). Details of the measurement were described in our related study (*5*).

In order to determine the hfd of the propane-d_1 (C_3H_7D) in the products of the early stage, an approximate method was adopted instead of using microwave spectrometry. The method is based on mean deuterium content obtainable by mass spectrometry, and the integrated ratio of methyl proton to methylenic proton obtainable by the NMR spectra (solvent: benzene). The procedure of calculation is explained in the Appendix. Signals of methyl proton and methylenic proton could be separated completely with a 100-mc/sec type NMR apparatus of Japan Electron Co. (JNM-4H 100), installed at the Faculty of Engineering Science, Osaka University, so

* CH_2DCHCH_2, CH_3CDCH_2, *cis*-CH_3CHCHD, and *trans*-CH_3CHCHD, where *cis* and *trans* denote the relative positions of the methyl and deuterium groups.

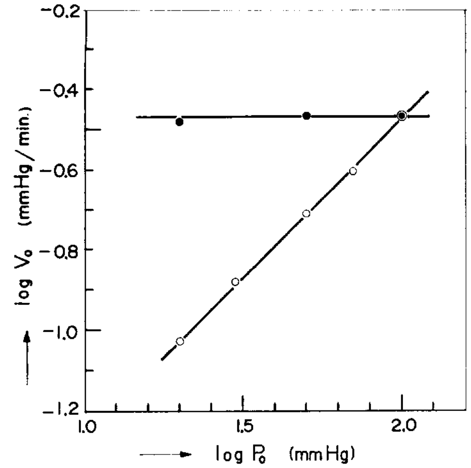


FIG. 1. Dependence of initial rate on the partial pressure of each reactant at 25°C: ○, $P_{C_3H_6}$ = 100 mm const.; ●, P_{H_2} = 100 mm const.

that the ratios of mean numbers of unsubstituted protons at both groups could be determined.

RESULTS

a. Kinetics. In order to estimate the pressure dependency of each reactant approximately, the initial rate of hydrogenation was investigated at 25°C, fixing the initial pressure of the other reactant at 100 mm. The initial pressure of propene showed practically no effect on the rate over the pressure range between 20 and 100 mm, while the initial pressure of hydrogen affected the rate clearly. In Fig. 1 the initial rate V_0 is plotted against the initial partial pressure on a log–log scale. From the gradient of the line, the following kinetic formula could be obtained, k_0 being the constant:

$$V_0 = k_0 P_{H_2}^m P_{C_3H_6}^n \qquad (1)$$

where

$m = 0.8;\ P_{C_3H_6} = 100,\quad P_{H_2} = 20\text{–}100$ mm
$n = 0;\quad P_{H_2} = 100,\ P_{C_3H_6} = 20\text{–}100$ mm

It might be pointed out that this type of pressure dependency was qualitatively found in the case of ethylene hydrogenation by the static method at 0° and 20°C on copper (*6*). This finding suggests that the hydrogenation mechanisms of ethylene and propene may probably be the same.

b. Exchange reaction. The experiments were carried out at 25° or 35°C with the gaseous mixture (P_{D_2}:$P_{C_3H_6}$ = 1:2). To begin with, fine distribution of the deuterated propenes was measured at various conversions. The results are summarized in Table 1,

TABLE 1
FINE DISTRIBUTION OF THE DEUTEROPROPENES

Expt. no.	Conversion (%)	Reaction temp. (°C)	Time (hr)	Fine distribution					ψ (%)
				d_0	d_1	d_2	d_3	d_4	
10	10	25°	1.3	$85._7$	$13._9$	$0._4$	—	—	2.4_5
32, 33, 34[a]	16	25°	2.7	$78._8$	$20._6$	$0._6$	—	—	3.6_3
12	20	25°	2.6	$74._1$	$24._4$	$1._5$	—	—	4.5_7
11	30	25°	3.9_5	$67._5$	$29._4$	$3._1$	—	—	5.9_3
37, 38[a]	30	25°	5.5	$65._8$	$31._3$	$2._9$	—	—	6.1_8
15	40	25°	5.3	$61._0$	$33._7$	$5._0$	$0._3$	—	7.4_3
23	40	25°	6.5	$59._9$	$35._5$	$4._2$	$0._4$	—	7.5_2
16	55	25°	8.1	$53._6$	$35._9$	$9._0$	$1._5$	—	9.7_3
39	55	25°	11.0	$52._9$	$38._4$	$7._7$	$1._0$	—	9.4_7
8	70	25°	11.0	$48._5$	$36._7$	$12._3$	$2._5$	—	$11._5$
31	85	25°	$20._7$	$44._0$	$38._2$	$13._9$	$3._3$	$0._6$	$13._1$
19	10	35°	0.8	$79._3$	$19._9$	$0._8$	—	—	3.5_8
17	31	35°	2.5	$61._9$	$32._6$	$4._7$	$0._8$	—	7.4_0
20	40	35°	3.3	$58._2$	$34._8$	$6._1$	$0._9$	—	8.2_8
18	70	35°	6.8	$47._0$	$35._7$	$13._0$	$3._3$	$1._0$	$12._6$

[a] These experiments were carried out at the same conditions, and their fine distributions are the mean values.

TABLE 2
HFD (%) OF THE MONODEUTEROPROPENES AT 25°C

Expt. no.	Conversion (%)	CH_2DCHCH_2	CH_3CDCH_2	*cis*-CH_3CHCHD	*trans*-CH_3CHCHD
32, 34	16	$(1.5 \pm 0.1) \times 3$	89.9 ± 5.8	2.4 ± 0.2	3.1 ± 0.2
15	40	$(4.5 \pm 0.4) \times 3$	78.5 ± 5.1	3.3 ± 2.0	4.8 ± 1.4
16	55	$(7.3 \pm 0.1) \times 3$	65.4 ± 2.2	5.0 ± 0.2	7.7 ± 0.2
8	70	$(8.8 \pm 0.1) \times 3$	59.0 ± 1.5	7.1 ± 0.2	7.8 ± 0.2
Ni	80	$(12.1 \pm 0.7) \times 3$	40.7 ± 2.9	11.7 ± 1.8	11.4 ± 1.8
Pd	85	$(18.0 \pm 1.0) \times 3$	16.1 ± 2.4	13.4 ± 2.1	16.4 ± 1.5
Pt	~80	$(7.0 \pm 0.6) \times 3$	26.7 ± 3.6	13.1 ± 2.5	39.1 ± 3.3

which shows the exchange reaction of propene with deuterium. The mean deuterium content $\psi = \frac{1}{6}\Sigma i d_i$, where $i = 0, 1, 2, \ldots, 6$, calculated for each experiment indicates the degree of deuteration. The same notation will be used to indicate the degree of deuteration for propane, i.e., $\psi = \frac{1}{8}\Sigma i d_i$, where $i = 0, 1, 2, 3, \ldots, 8$.

In Fig. 2, fine distribution of the monodeuteropropenes at 25°C is plotted against the mean deuterium content ψ. The theoretical curves which are shown by full and dotted lines in Fig. 2 will be explained in the discussion.

Table 2 shows the hyperfine distribution of the monodeuteropropenes in percent for several experiments. In the table, corresponding data (*3*) on nickel, palladium, and platinum catalysts are compared with the present results on copper, though the experimental conditions were slightly different (Ni, 17°C; Pd, 20°C; Pt, 20°C). The peculiar result found on nickel was again observed on copper, i.e., methinic hydrogen is the most exchangeable at each conversion, while other kinds of hydrogens have a low and similar activity. Therefore, only the CH_3CDCH_2 species was detectable on samples at conversions below 40%, because the sensitivity of the apparatus which we used was so low that the determination of the other species was impossible. However, by a measurement kindly carried out by Dr. Shuji Saito of the Sagami Central Chemical Laboratory, Kanagawa Pref., the result at 16% conversion could be obtained. It is remarkable in this experiment that the amount of CH_3CDCH_2 species reaches nearly 90% (See Table 2).

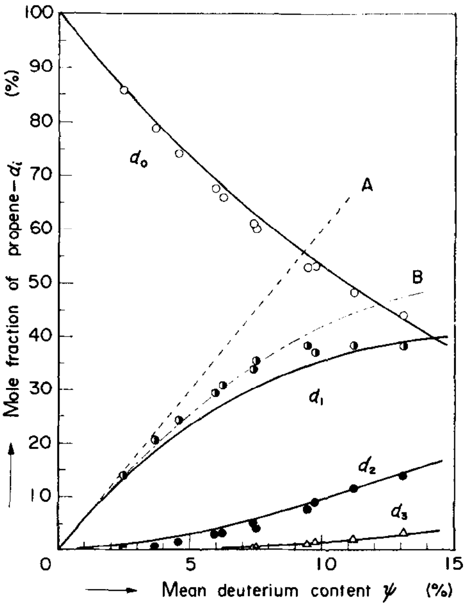


FIG. 2. Fine distribution of deuteropropenes vs. ψ. ($\psi = \frac{1}{6}\Sigma i d_i$): ———, random distribution, i.e., $d_i = {}_6C_i \cdot \psi^i (1 - \psi)^{6-i}$ ($i = 0, 1, 2, \ldots 6$); ○, ◑, ●, △, obs.

Another point to be mentioned is the fact that the amount of *trans*-CH_3CHCHD was practically equal to that of *cis* CH_3CHCHD as in the case of nickel, contrary to the case of platinum in which trans species were produced much more than cis species (*3*b).

c. Hydrogenation. Fine distribution of the deuteropropanes produced by the reaction is shown in Fig. 3. The fine distribution is very similar in shape to that of the deuteroethanes produced in the hydrogenation of ethylene (*7*). For example, d_0 % is larger than d_1 % at the initial stage, and the tendency becomes less marked as the reaction proceeds.

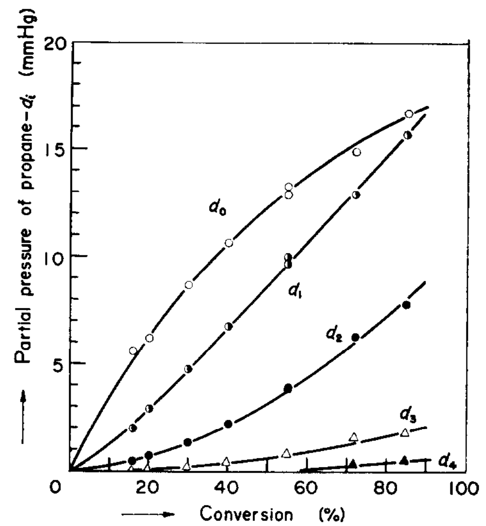


FIG. 3. Fine distribution of deuteropropanes in their partial pressures vs. conversion: ○, C_3H_8; ◑, C_3H_7D; ●, $C_3H_6D_2$; △, $C_3H_5D_3$; ▲, $C_3H_4D_4$.

As mentioned in the section on analysis, the hfd of the monodeuteropropanes was investigated semiquantitatively. According to Fig. 3, the larger part of the deuteropropanes was C_3H_7D below 70% conversion, but an amount of polydeuteropropanes that was not negligible still existed. It has to be admitted, therefore, that the hfd determinable from NMR spectra would be an approximate one. Spectra of pure propane and sample No. 39 are shown in Fig. 4. From these spectra, the ratio of deuterium substituted at the two groups of propane was calculated by the procedure described in the Appendix. The results are summarized in Table 3, though the mean deviation of the measured values is large.

Table 3 indicates that deuterium atoms seem to attack the central carbon more easily than the terminal carbons of propene. Though the data corresponding to 10% conversion (No. 10) may give more important support to the conclusion, its measurement could not be done with sufficient accuracy, because of the small amount of the samples. However, considering the situation that the number of hydrogens at the central carbon is three times smaller than that at the two terminal carbons, there is no doubt that hydrogen at the central methine group is more active than that at the methylene group. This interesting result plays a role in assuming the chemisorbed species on copper. Of course, this inclination cannot be shown conspicuously as the reaction proceeds, judging from the decrease of the ratio of D% in the CH_2 group to D% in the CH_3 groups, as shown by Table 3.

d. Self-hydrogenation. Propene alone was introduced into the reaction tube for 5 hr or for 19 hr at 25°C. No detectable propane was observed in either case by either gas chromatographic or mass spectrometric methods,

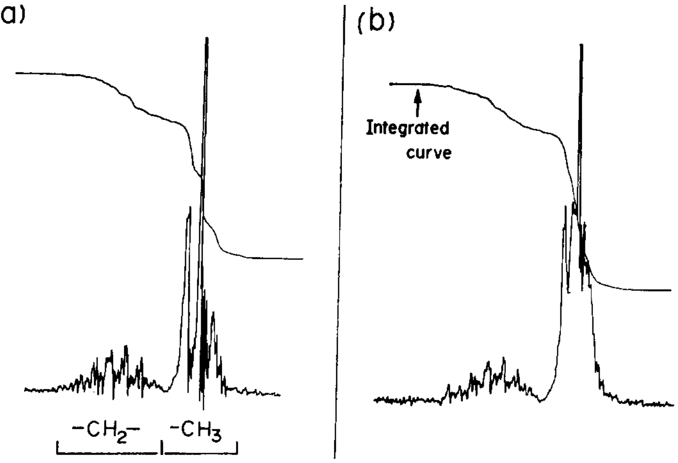


FIG. 4. NMR spectra of propane: (a) "light" propane (propane-d_0); (b) propane produced in Expt. 39, containing propane-d_0, -d_1, -d_2, and -d_3.

TABLE 3

Distribution (%) in the Deuteropropanes, at 25°C

No.: Conversion (%):	32, 33, 34[a] 16	37, 38[a] 30	23 40	39 55
D % in —CH_3 groups	39 ± 10	33 ± 5	46 ± 4	55 ± 4
D % in —CH_2- group	61 ± 10	67 ± 5	54 ± 4	45 ± 4

[a] Mean values of three and two runs carried out at the same experimental conditions, because the amount of the sample obtainable in one experiment was too small.

so that the amount of dissociative species of propene may be negligibly small, if the species exists on the surface.

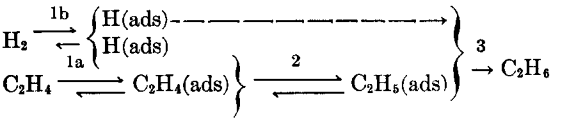
Discussion

A. *Associative Mechanism*

In our previous reports (*3a*, *8*), it was concluded that the hydrogenation of propene [Eq. (2)]

$$C_3H_6 + H_2 \rightarrow C_3H_8 \qquad (2)$$

on nickel obeys the standard associative mechanism of Horiuti and Polanyi (*9*), which can be formulated for ethylene by Eq. (3), where H(ads) indicates the adsorbed hydrogen, and so on.



(3)

The length of each arrow in Eq. (3) is drawn so as to qualitatively correlate the relative magnitude of the rates when steady state is reached. Moreover, the net rate in each step is indicated by making differences of the length of arrows to be equal. The back reaction of step 3 is neglected provisionally, considering the large exothermic heat of the process. Other details of the relative values of the rates will be discussed below. The reaction scheme shown by Eq. (3) can explain easily the results (*7*) of fine distribution in both deuteroethylenes and deuteroethanes, as shown by Keii (*10*).

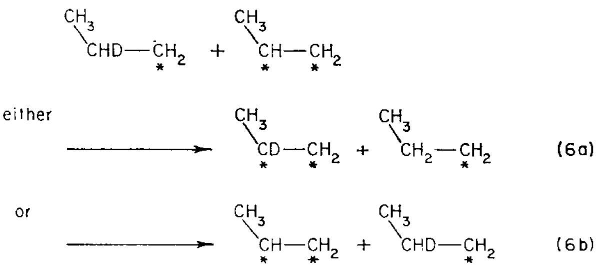
It might be mentioned here why the scheme of Eq. (3) was adopted rather than the one modified by Twigg and Rideal (*11*), who did not favor step 1b and adopted Eqs. (4) and (5) as the source of H(ads) or D(ads) on a metal surface.

$$\underset{*}{C}H_2\text{—}\underset{*}{C}H_2 + D_2 \rightarrow \underset{*}{C}H_2\text{—}CH_2D + \underset{*}{D} \qquad (4)$$

$$\underset{*}{C}H_2\text{—}CH_2D \rightarrow \underset{*}{C}H_2\text{—}\underset{*}{C}HD + \underset{*}{H} \qquad (5)$$

In Eqs. (4) and (5), asterisks are used for adsorbed species, in order to indicate clearly the bonding to the catalyst.

This modified scheme may also explain the predominant occurrence of C_3H_8 at the early stage of hydrogenation of propene (Fig. 3), if H(ads) attacks C_3H_7(ads), which is produced by the reaction of C_3H_6(ads) with H(ads), more easily than C_3H_6D(ads). However, in order to fulfill such a condition, a special assumption which is not evident must be required, i.e., Eq. (6a) occurs much more easily than Eq. (6b).



(6a)

(6b)

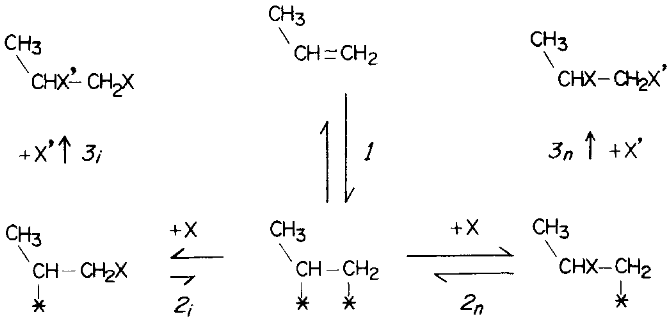


FIG. 5. Extended associative scheme of propene hydrogenation: X, X′ H or D adsorbed on surface. Length of arrows designates the relative rate of steps qualitatively.

This is the detailed reason, besides the sake of simplicity, why the authors considered that the scheme of Eq. (3) is more plausible on nickel, even though there is some experimental and theoretical evidence for the Twigg-Rideal scheme in ethylene hydrogenation (*12*).

Now, the associative mechanism may also be applied to the reaction on copper, because the catalytic activity of copper resembles very much that of nickel, judging from the hfd of monodeuteropropene; i.e., as Table 2 shows, methinic hydrogen is the most exchangeable, and the amounts of cis and trans species are practically equal at every stage of the reaction. The reason why the pressure of propene is not included in Eq. (1) is expected from the assumption that propene is chemisorbed nearly to saturation. However, it is very probable that on the copper surface there still remain enough chemisorbable sites where hydrogen can be accommodated as atoms. This presumption will be adopted implicitly in the present discussion.

These findings are consistent with the standard associative mechanism that step 3 in Eq. (3) is the slowest step* in the total reaction.

B. *Extended Associative Mechanism*

When Eq. (3) is applied to higher olefins, an unresolved problem arises regarding the bonding of the propyl species to the catalyst. This was pointed out in our previous reports (*3*a, *8*). But the problem may be solved easily by extending the associative mechanism as shown by Fig. 5, where the relative rate of each step is designated qualitatively. The extended part of the scheme lies in the point that step 2 in Eq. (3) is divided into two steps, 2_n and 2_i, according to the formation of *n*-propyl and isopropyl species, respectively. Correspondingly, step 3 is also divided into two steps, 3_n and 3_i. The rate of step 3_n must be equal to the difference between the rates of the forward and back steps of 2_n, and a similar relation must exist between step 3_i, and forward and back steps 2_i.

In this scheme, the rates of the forward and back processes of step 2_n are assumed to be faster than those of step 2_i (see below). This assumption is due to the result that CH_3CDCH_2 produced by step 2_n is the major species of all the monodeuteropropenes in Table 2. It will be useless to mention that both CH_3CHCHD species are produced by step 2_i.

Formation of the CH_2DCHCH_2 species shown in Table 2 can be explained by a kind of double-bond migration via the 2_i process, as already proposed (*7*). The finding that the percentages of CH_2DCHCH_2 and *trans*- and *cis*-CH_3CHCHD in Table 2 are nearly equal per hydrogen atom can be explained easily, if the processes of Eq. (7) occur.

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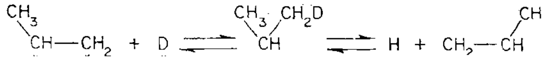
* In the present paper, the slowest step is defined so that the forward rate of the step is the smallest of all the steps. This technical term was adopted in order to avoid the use of the term "rate-determining step," which has a special definition in the modified associative mechanism of Horiuti (*9*b).



$$CH_3CH{-}CH_2 + D \rightleftharpoons (CH_3)(CH_2D)CH \rightleftharpoons H + CH_2{-}CH(CH_2D) \qquad (7)$$

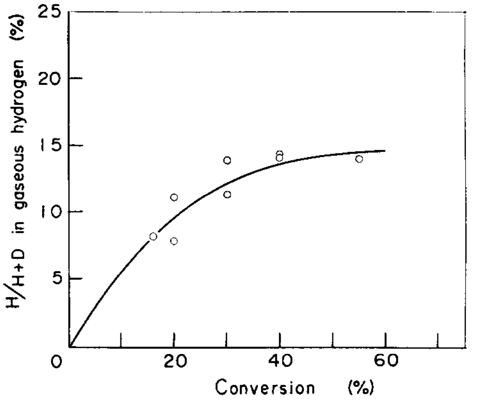
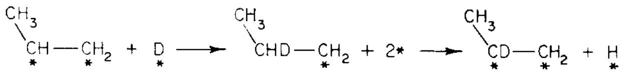


FIG. 6. Fraction of protium in the gaseous hydroen vs. conversion.

In the steady state of reaction, it can be regarded that the deuterium concentration of the central CH_2 group in the *n*-propyl species is in quasi-equilibrium with the surface hydrogen pool which consists of adsorbed H and D atoms, even if the deuterium concentration of the terminal CH_3 groups in the isopropyl species is not in quasi-equilibrium. The deuterium concentration in the pool would be small at the initial stage, because the rates of the back and forward processes of step 2_n are sufficiently large and chemisorbed propene is larger than chemisorbed hydrogen in amount, in accordance with the essential feature of the associative mechanism; i.e., H(ads) is produced by Eq. (8) so easily that the amount of C_3H_7(ads) produced is much larger than expected in the case when Eq. (8) does not proceed so fast. This tendency, in turn, offers the reason why C_3H_8 is produced much more than expected. Moreover, production of C_3H_8 would become more favorable if the addition of H(ads) to the C_3H_7(ads) occurs more favorably for H than for D in step 3, even though the isotopic effect can be negligibly small in step 2_n and step 2_i.


$$\underset{*}{\overset{\mathrm{CH_3}}{\mathrm{CH}}}-\underset{*}{\mathrm{CH_2}}+\underset{*}{\mathrm{D}}\longrightarrow\overset{\mathrm{CH_3}}{\mathrm{CHD}}-\underset{*}{\mathrm{CH_2}}+2*\longrightarrow\underset{*}{\overset{\mathrm{CH_3}}{\mathrm{CD}}}-\underset{*}{\mathrm{CH_2}}+\underset{*}{\mathrm{H}}\qquad(8)$$

The back rate of step 1b at the initial stage was estimated from the ratio of protium to deuterium appearing in the gas phase. The ratio was calculated from the material balance of deuterium and the result is plotted against conversion in Fig. 6. This figure shows that the protium appearing in the gaseous hydrogen is not negligible. This offers the reason why the back rate of step 1b cannot be neglected in the steady state, and also why step 1b cannot become the slowest in the total reaction scheme.

As already mentioned, step 2_n is faster than step 2_i. If the difference of their rates is very large so that only step 2_n reaches quasi-equilibrium, it may be expected that the D atom enters into the central and terminal groups of the propane produced in the ratio of 2 to 1 at the initial stage. This expectation is shown to be correct by the data at low conversion in Table 3, which give approximately the hfd of monodeuteropropanes. Of course, as the conversion becomes high, the contributions of steps 2_i and 3_i increase, and the amount of the deuterium atom entering into the terminal groups becomes larger. This tendency is shown above 55% conversion.

The finding that the d_0 species is major in the produced propanes explains why the hydrogenation step of the half-hydrogenated species becomes the slowest. Besides, crossing of the curves of d_0 and d_1 species occurs at higher conversion in the propene hydrogenation (see Fig. 3) than in the ethylene hydrogenation (7) using the reactant in the ratio of ethylene to deuterium, 1:1. This is probably another evidence that deuterium concentration on the surface is small, i.e., X and X′ in the reaction scheme are mostly H but not D, due to the fact that olefin-to-deuterium ratio in the initial reactants is 2 in the present research.

As a generalized mechanism, it may be more clever to take the dissociative species as well as the π-adsorbed species of propene into consideration. Formation of the dissociative species which was proposed on platinum (3b) can, however, be ruled out, because *cis*- and *trans*-propene-d_1 are practically equal in amount, as shown in Table 2. Be-

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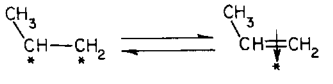
* In the previous reports, both processes producing *n*-propyl and isopropyl species were denoted by 2β and 2α, respectively, instead of 2_n and 2_i, as now defined.

sides, the possibility of dissociation of propene on copper can also be ruled out by the result on self-hydrogenation described in the last part of the experiment under the same conditions as the present hydrogenation. Concerning the π-adsorbed species, there is no positive and inevitable reason to take it into consideration so as to explain the experimental result, even though the species may exist in equlibrium with the associative species, as Eq. (9) indicates.



(9)

C. *The Random-Distribution Law in Determining the Number of Exchangeable Hydrogens*

For the sake of reference, the random-distribution law (*13*) was applied to the result of the present exchange reaction, because the law has been used often in order to determine whether all the hydrogens concerned have equal activity in deuterium exchangeability or not. By comparing the experimental points on deuteropropenes with the curves in Fig. 2, which were calculated by the random-distribution law, an unexpected result was obtained; i.e., if a small deviation of the d_1 species can be disregarded, the plots of the d_0, d_2, and d_3 species lie fairly well on the curves. However, considering that the hfd of the d_1 species requires that methinic hydrogen at least is more exchangeable than the others, the law may not necessarily be applied to the hydrogens under consideration. Therefore, the small deviation of the d_1 species from the calculated curve cannot be neglected, but rather has much significance in discussing the exchange mechanism.*

In order to investigate the problem in detail, the $d_1\%$ was calculated again, assuming that only one or two hydrogens in propene are exchangeable, and the results are plotted, respectively, as dashed lines A and B, in Fig. 2. It is interesting that the observed values lie on line B very well rather than line A, though only the methinic hydrogen is the most exchangeable of all the six hydrogens. Thus, without the knowledge of the hfd of monodeuteropropenes, it would have been concluded that the random-distribution law is applicable, and two hydrogens in propene have higher activity in deuterium exchange than the other four hydrogens. This means that, even if detailed investigations are carried out, there is a possibility of drawing an erroneous conclusion on the basis of the distribution law.

The incorrect conclusion derivable from the use of the random-distribution law calls attention to using it to determine the number of exchangeable hydrogens of the same activity. This, in turn, should teach us the necessity of studying hyperfine distribution in addition to the usual distribution of the deuterated products, in order to investigate the reaction mechanism by use of deuterium tracers.

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APPENDIX

Determination of Mean Deuterium Fraction of Methylenic Group in Deuteropropane from NMR Spectra

Integrals of NMR spectra give us the ratio of methyl protons to methylenic protons in given samples. The observed ratio, S, is given by Eq. (A1).

$$S = \frac{\text{total protons in methyl group}}{\text{total protons in methylenic group}} \quad \text{(A1)}$$

If the sample consists of C_3H_8, S would be 3 and signals of both groups consist of 3 and 7, respectively. If the mean fraction of deuterium atoms in the methylenic group of deuterated propane is X %, the number of deuterium atoms at both groups in 100 propane molecules is given by Eqs. (A2).

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* The data at 35°C deviate also from the theoretical curve, though they were not plotted in order to avoid the figure becoming too complex.

D atoms in methyl group

$$= \frac{100 - X}{100} \sum_{i=1}^{8} id_i$$

D atoms in methylenic group

$$= \frac{X}{100} \sum_{i=1}^{8} id_i \qquad \text{(A2)}$$

where d_i is the molar fraction of d_i species of propane observed with mass spectrometry. Therefore, the number of protium atoms at both positions in 100 propane molecules can be given by Eqs. (A3), respectively.

H atoms in methyl group

$$= 600 - \frac{100 - X}{100} \sum id_i$$

H atoms in methylenic group

$$= 200 - \frac{X}{100} \sum id_i \qquad \text{(A3)}$$

Substituting Eqs. (A3) in Eq. (A1), S can be expressed by Eq. (A4)

$$S = \frac{600 - [(100 - X)/100]\Sigma id_i}{200 - (X/100)\Sigma id_i} \qquad \text{(A4)}$$

Thus, X can be given in % by Eq. (A5)

$$X = \frac{200(S - 3) + \Sigma id_i}{(1 + S)\Sigma id_i} \times 100 \qquad \text{(A5)}$$

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