JOURNAL OF CATALYSIS **102**, 377–385 (1986)

Mechanism of Deuterium Addition and Exchange of Propene over Pd/SiO$_2$ at Lower Temperatures: Direct Evidence for Intramolecular Double Bond Migration during Hydrogenation

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Received February 15, 1986; revised July 8, 1986

The mechanism of the deuterium addition and exchange reaction of propene over Pd/SiO$_2$ at lower temperatures was elucidated by applying microwave spectroscopy as well as kinetic study. The activation energies for the exchange of each hydrogen in propene and for the deuterium addition were determined. In the absence of deuterium molecule, the hydrogen exchange reaction proceeds via dissociative mechanism including *n*-propenyl, sec-propenyl, and allylic adsorbed species. In the presence of gaseous deuterium molecules, however, both addition and exchange processes proceed via associative mechanism involving *n*-propyl as well as sec-propyl species; the methyl groups of the latter species are not equivalent for abstraction of a hydrogen atom. In addition, direct evidence was obtained for the intramolecular double bond migration process during hydrogenation, which may proceed via an intermediate with a bridged hydrogen between C$_1$ and C$_3$ carbons of propene. © 1986 Academic Press, Inc.

INTRODUCTION

It has been generally accepted that hydrogenation of olefins over transition metal catalysts proceeds via associative mechanism (Horiuti–Polanyi mechanism) through σ-alkyl intermediates (*1*). In this mechanism, hydrogen exchange and isomerization of olefins are explained to proceed by the reverse reaction of σ-alkyl species formation. On the other hand, since olefin molecules are easily adsorbed dissociatively on metal surfaces (*2*), it is often considered that this dissociatively adsorbed species may also be the intermediates for hydrogen exchange and isomerization processes (dissociative mechanism, originally proposed by Farkas *et al.* (*3*)). Although many mechanistic studies on these processes have been reported (*4–6*), some controversy seems to exist in the literature when associative or dissociative mechanisms are applied to the hydrogen exchange and isomerization processes (*7, 8*).

Palladium metal is one of the most efficient catalysts for the selective hydrogenation of various organic compounds, and its catalytic behavior and reaction mechanisms have been extensively studied (*9–14*). Hirota and Hironaka applied microwave spectroscopic technique to study C$_3$H$_6$–D$_2$ reaction over palladium metal and observed that all the hydrogens in propene were equally exchangeable (*15*). They proposed the existence of some dissociative species in addition to the σ-alkyl associative one in equilibrium with the former.

On the other hand, palladium metal tends to form allylic species by abstracting hydrogen from olefin (dissociative mechanism) (*16, 17*). Gault *et al.* investigated the exchange and isomerization of butene on an evaporated film of palladium at 273 K, using perdeuteropropene as a deuterating agent (*18*). From the microwave spectroscopic analysis of monodeuterobutene, they introduced dissociatively adsorbed allylic species as the main intermediate for the exchange and double bond migration. They also proposed an associative Horiuti–Polanyi mechanism for *cis–trans* isomerization of butene even in the absence of gas-

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eous hydrogen. In addition they examined the exchange and isomerization of butene in the presence of deuterium and found that the reaction rate was much faster than that for the reaction with perdeuteropropene (*19*). They considered that the exchange and isomerization processes proceeded through an allylic type intermediate and attributed the enormous acceleration effect of gaseous deuterium to the increase in the number of such active sites as corners and edges induced by deuterium molecules.

Under these circumstances we felt it important to clarify the correlation of these two extreme mechanisms: associative and dissociative mechanism in the presence and absence of gaseous hydrogen. For this purpose, we compared the kinetics of the C_3H_6–D_2 reaction with that of the C_3H_6–C_3D_6 reaction over Pd/SiO_2 at lower temperatures. The time course of isotopic distribution in formed monodeuteropropene was followed by microwave spectroscopy. The kinetics as well as the activation energies of these reactions were considerably different and it was concluded that associative and dissociative mechanisms should not be adopted at the same time. We also found the direct evidence for the intramolecular isomerization process during the hydrogenation of propene (C_3H_6–D_2 reaction), which may be the key process to solve the discrepancy of the previous conclusions. The mechanism of this process is discussed in detail to propose the possible structure of intermediate.

METHODS

Supported palladium catalyst was prepared by a conventional impregnation method of precursor salt (5 wt%, H_2PdCl_4) on SiO_2 powder (Aerosil) (*20*). After drying for 4 h at 373 K in an oven, 0.2 g of the catalyst was placed in a U-shaped vessel, which was connected to an all-glass enclosed gas circulation system. It was reduced by hydrogen at 773 K for 20 h, with a liquid-nitrogen cold trap to collect HCl and H_2O. The dispersion of Pd metal on the support was determined to be 8.2% by the H_2–O_2 titration method at room temperature (*21, 22*). Absence of surface impurities on the reduced catalyst was confirmed by XPS (VG, Escalab 5), except for a small amount of residual chloride.

H_2 and D_2 gases from commercial cylinders were purified by circulating over a heated Pd black catalyst to remove trace amount of oxygen. C_3H_6 purchased from Takachiho Kagaku KK and C_3D_6 from Merck, Sharp & Dohme LTD were purified by a freeze–thaw cycle. $CHD{=}CH{-}CH_3$ was prepared from 1-bromo-1-propene according to a procedure described by Norris (*23*).

The reaction was carried out in the enclosed gas circulation system mentioned above (total volume: 310 cm^3). Before each run the Pd/SiO_2 catalyst was freshly reduced by H_2 or D_2 at 473 K during 2 h and cooled down to the reaction temperature without evacuating hydrogen gas. A certain amount of propene was introduced into the system and the reaction was started. The reaction temperature was maintained by suitable cold slush baths such as H_2O–MeOH, dry ice–MeOH, isopropanol, acetone, and ethanol. A small amount (a few percents) of the reaction gas was sampled at certain intervals during the reaction and separated into propane and propene by gas chromatography (alumina column, He carrier). Deuterium contents in formed propane and exchanged propene were determined by mass spectrometry (Hitachi RMU-6MG) with the ionization voltage of 13 and 15 eV, respectively. The location of the deuterium atom in monodeuteropropene was determined by recording the microwave absorption lines characteristic of each isotopic species. The microwave spectrometer was of a conventional 110-kHz sine-wave Stark modulation type. The cell was made of a rectangular copper wave guide 3 m in length. It was cooled by dry ice during the measurement. The microwave from an X-band klystron was frequency-doubled to measure the 1_{01}–0_{00} rotational

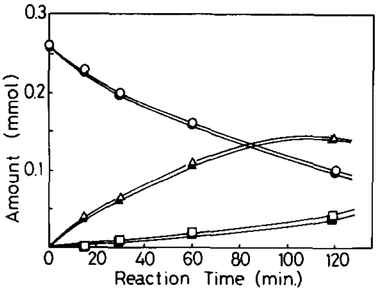


FIG. 1. Time courses of C_3H_6–C_3D_6 reaction over Pd/SiO_2 at 227 K. $P_{C_3H_6} = P_{C_3D_6}$ = 15 Torr, catalyst = 0.2 g. (○) C_3H_6, (△) C_3H_5D, (□) $C_3H_4D_2$, (■) $C_3H_2D_4$, (▲) C_3HD_5, (●) C_3D_6.

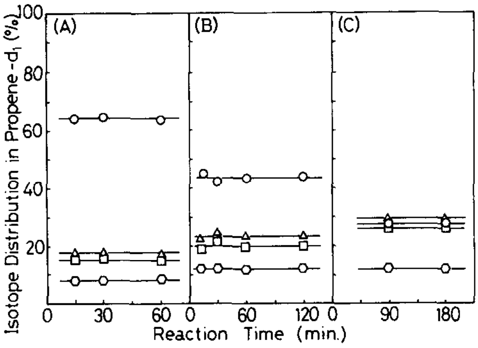
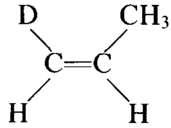
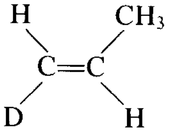


FIG. 2. Time courses of isotope distribution in propene-d_1 during C_3H_6–C_3D_6 reaction over Pd/SiO_2 at various temperatures. $P_{C_3H_6} = P_{C_3D_6}$ = 15 Torr, catalyst = 0.2 g; (A) 249 K, (B) 227 K, (C) 198 K. (□) c-1-d_1, (△) t-1-d_1, (○) 2-d_1, (○) 3-d_1.

transitions. The detailed procedures were reported previously (*24*). The notations for isotopic isomers in monodeuteropropene are: *cis*-1-d_1,



; *trans*-1-d_1,



; 2-d_1, $CH_2{=}CD{-}CH_3$; 3-d_1, $CH_2{=}CH{-}CH_2D$.

RESULTS

C_3H_6–C_3D_6 Reaction

Figure 1 shows the amounts of various propenes as functions of time during the reaction between propene and perdeuteropropene at 227 K. A mixture of C_3H_6 and C_3D_6 (1 : 1, 15 Torr each, 1 Torr = 133.3 N m^{-2}) was introduced onto a Pd/SiO_2 catalyst and the amounts of hydrogen-exchanged propene were followed. As the reaction proceeded, same amounts of C_3H_5D and C_3HD_5 were formed with corresponding decrease of C_3H_6 and C_3D_6. The amounts of doubly exchanged species increased significantly only after the amount of C_3H_5D and C_3HD_5 reached the maximum. This result indicates the stepwise exchange in the reaction between propene molecules. Figure 2 demonstrates the microwave spectroscopic analyses of the deuterium distribution in monodeuteropropene at three different temperatures. At the initial stage of the reaction where monodeuteropropenes are main reaction products the isotope distribution stayed unchanged. However, the mutual ratio depended considerably upon the reaction temperature. At 249 K, more than 60% of monodeuteropropene was $CH_2{=}CH{-}CH_2D$ (3-d_1), whereas the relative amount of this species considerably decreased at lower temperatures with the corresponding increase of $CHD{=}CH{-}CH_3$ (*cis*- and *trans*-1-d_1). This finding suggests that each d_1 species is formed through a different reaction intermediate.

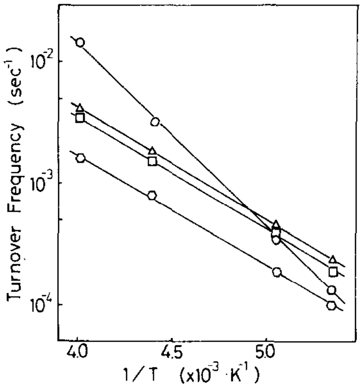


FIG. 3. Arrhenius plots of the initial rates of the formation of propene-d_1 isomers during C_3H_6–C_3D_6 reaction over Pd/SiO_2. $P_{C_3H_6} = P_{C_3D_6}$ = 15 Torr, catalyst = 0.2 g. (□) c-1-d_1, (△) t-1-d_1, (○) 2-d_1, (○) 3-d_1.

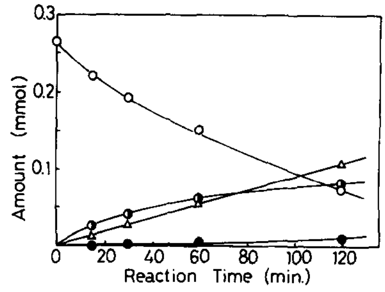


FIG. 4. Time courses of C_3H_6–D_2 reaction over Pd/SiO_2 at 187 K. $P_{C_3H_6}$ = 15 Torr, P_{D_2} = 30 Torr, catalyst = 0.2 g. (○) C_3H_6, (◐) C_3H_5D, (●) $C_3H_4D_2$, (△) propane.

The Arrhenius plots for these processes are displayed in Fig. 3, where the rates are expressed in terms of turnover frequency (the number of propene molecules formed on one surface palladium atom in a second). The number of surface Pd atoms was estimated from the result of dispersion measurement. The apparent activation energy for the exchange reaction of each hydrogen in propene was determined from the slopes of the plots. The hydrogen atoms attached to the double-bond carbons exhibited similar activation energies: 1-d_1, 4.5 kcal mol^{-1} and 2-d_1, 4.3 kcal mol^{-1}. However, the activation energy for the hydrogen atom in the methyl group was much larger (3-d_1, 7.0 kcal mol^{-1}).

C_3H_6–D_2 Reaction

A mixture of D_2 (30 Torr) and C_3H_6 (15 Torr) was introduced onto a Pd/SiO_2 catalyst at 187 K. Both deuterium addition and exchange reactions took place simultaneously as shown in Fig. 4. The main product of the exchange process was C_3H_5D. Since the amount of $C_3H_4D_2$ was small at the initial stage of the reaction, the exchange process seemed to proceed successively.

The temperature dependence as well as the pressure dependence of these processes were investigated by measuring the reaction rates for temperature between 227 and 165 K, for D_2 partial pressures between 30 and 200 Torr (with constant pressure of C_3H_6, 15 Torr), and for C_3H_6 partial pressures between 7.5 and 30 Torr (with constant D_2 pressure, 50 Torr). The results are illustrated in Figs. 5 and 6. It can be seen that the curves are parallel for hydrogenation and exchange processes: E_a(hyd.) = 9.3 kcal mol^{-1} and E_a(exc.) = 9.1 kcal mol^{-1}; V(hyd.) = $kP_{D_2}^{0.6}P_{C_3H_6}^{0}$ and V(exc.) = $k'P_{D_2}^{0.6}P_{C_3H_6}^{0}$. These results strongly suggest

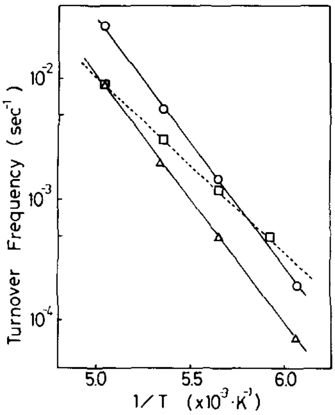


FIG. 5. Arrhenius plots of the initial rates of C_3H_6–D_2 and C_3H_5D–H_2 reactions over Pd/SiO_2. (○) Initial rates of C_3H_5D formation in the exchange process of C_3H_6–D_2 reaction; (△) initial rates of propane formation in the addition process of C_3H_6–D_2 reaction; (□) initial rates of 3-d_1 formation in double bond migration process of C_3H_5D–H_2 reaction. P_{propene} = 15 Torr, P_{hydrogen} = 30 Torr, catalyst = 0.2 g.

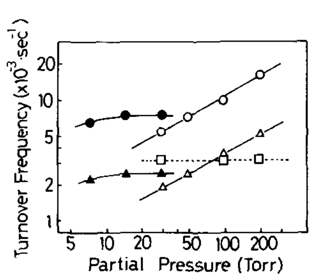


FIG. 6. Pressure dependence of the initial rates of C_3H_6–D_2 and C_3H_5D–H_2 reaction over Pd/SiO_2 at 187 K (catalyst = 0.2 g). Open symbols: dependence upon P_{D_2} or P_{H_2} ($P_{C_3H_6}$ = 15 Torr). Closed symbol: dependence upon $P_{C_3H_6}$(P_{D_2} = 50 Torr). (○,●) Initial rates of C_3H_5D formation in C_3H_6–D_2 reaction; (△,▲) initial rates of propane formation in C_3H_6–D_2 reaction; (□) initial rates of 3-d_1 formation in C_3H_5D–H_2 reaction.

TABLE 1

Isotope Distribution of Propane, Propene, and Hydrogen during C_3H_6–D_2 Reaction over Pd/SiO_2 at 187K (P_{D_2} = 30 Torr, $P_{C_3H_6}$ = 15 Torr)

	Propane (%)	Propene (%)	Hydrogen (%)	Propane (%)	Propene (%)	Hydrogen (%)	Propane (%)	Propene (%)	Hydrogen (%)
Reaction time:		10 min			20 min			80 min	
Conversion (%)	4.4	95.6		11.8	88.2		33.7	66.3	
d_0	28.8	90.2	1.4	29.7	82.6	2.2	28.5	58.8	3.9
d_1	30.5	8.8	4.3	32.2	15.2	9.6	31.6	30.4	22.1
d_2	34.4	1.1	94.4	27.4	2.1	88.2	26.5	8.8	74.0
d_3	4.5	0		7.5	0		9.2	2.6	
d_4	1.8	0		1.7	0		2.6	0	
d_5	0	0		0	0		0	0	
d_6	0	0		0	0		0	0	
d_7	0			0			0		
d_8	0			0			0		

that both processes proceed through the same reaction intermediate, presumably through the σ-alkyl species (associative mechanism).

Table 1 summarizes the deuterium distribution of propane, propene and hydrogen during C_3H_6–D_2 reaction over Pd/SiO_2. As can be seen from the table and Fig. 4, the deuterium exchange process of propene seems to be stepwise, which corresponds well to the increase of HD and H_2 in the gas phase. On the other hand, the isotopic distribution of the formed propane was in a different situation. Almost the same amounts of C_3H_8, C_3H_7D, and $C_3H_6D_2$ were formed during the reaction, which indicates that the surface H/D ratio available for hydrogenation is almost unity and quite different from the isotopic ratio in the gaseous hydrogen.

Figure 7 shows the overall composition of monodeuteropropenes formed in this reaction. It is evident that a considerable change in the isotope distribution occurred. If the exchange process proceeds through the σ-alkyl intermediate alone, as has been suggested in the earlier paragraph, the rate of the formation of 2-d_1 from *n*-propyl and those of 1-d_1 and 3-d_1 from sec-propyl species should stay constant at the initial stage of the reaction where isotope dilution of deuterium by the repetition of the associative mechanism is not significant (*25*). Accordingly, drastic change in isotope distribution of monodeuteropropene in Fig. 7 indicates that some additional mechanism for the exchange process is operating beside the associative one. The most probable mechanism is an intramolecular hydrogen shift between C_1 and C_3 carbons, as discussed in a later section.

C_3H_5D–H_2 reaction

To confirm the intramolecular isomerization mechanism mentioned above, the reaction between propene 1-d_1 and H_2 was carried out under a condition similar to that of the C_3H_6–D_2 reaction. In the present reaction, deuterium exchange by the repetition of the half-hydrogenated state can be ne-

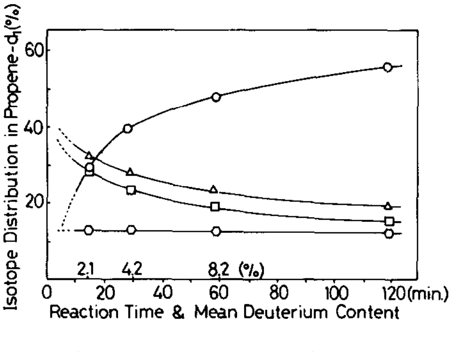


FIG. 7. Time courses of isotope distribution in propene-d_1 during C_3H_6–D_2 reaction over Pd/SiO_2 at 187 K. $P_{C_3H_6}$ = 15 Torr, P_{D_2} = 30 Torr, catalyst = 0.2 g. (□) c-1-d_1, (△) t-1-d_1, (○) 2-d_1, (O) 3-d_1.

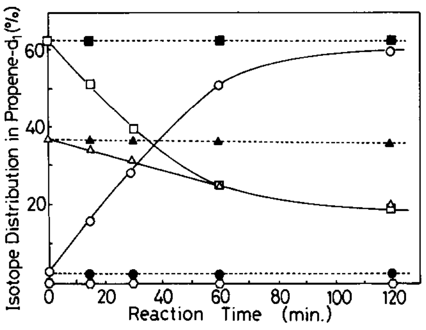


FIG. 8. Time courses of isotope distribution in propene-d_1 during C_3H_5D–H_2 reaction over Pd/SiO_2 at 187 K. (□) c-1-d_1, (△) t-1-d_1, (○) 2-d_1, (○) 3-d_1. $P_{C_3H_5D}$ = 15 Torr, P_{H_2} = 30 Torr, catalyst = 0.2 g. See text.

glected and only the double bond migration process can be followed because of the isotopic ratio of H and D (30 : 1) present in the system. Isotope distribution change of monodeuteropropene measured by microwave spectroscopy, shown in Fig. 8, which is similar to Fig. 7, indicates the existence of the intramolecular 1,3-hydrogen shift during the hydrogenation of propene on Pd metal. The broken lines in the figure represent the result in the absence of gaseous H_2. When ony C_3H_5D was introduced onto the hydrogen-preadsorbed surface, the double bond migration process proceeded, until adsorbed hydrogen was exhausted by hydrogenation. Thus this process requires H_2 in the gas phase.

Figure 5 shows the temperature dependence of this process. The activation energy was obtained to be 7.0 kcal mol^{-1}. The dependence of the rate upon the partial pressure of H_2 was very slight as shown in Fig. 6. These results indicate that the reaction intermediate for the double bond migration process is different from that for hydrogenation and exchange.

DISCUSSION

Microwave spectroscopy is a powerful technique for the study of hydrogen exchange or isomerization reaction of propene or butene (*26*). It enables us to determine the hyperfine distribution of the D atoms in the exchanged d_1-molecule. The location of the D atoms in the products revealed the previous points of attachment of the adsorbed molecules to the catalysts. Another important merit of this method lies in the fact that the time course of production of different deuterium-substituted species can separately be followed by the measurement of the intensity of microwave absorption lines of each species (*5*). Hence we can extrapolate the deuterium isotope distribution into the value at time zero.

As mentioned already, Hirota and Hironaka (*15*) and Gault *et al.* (*18*) applied this method to the study of hydrogen exchange and isomerization of propene or butene over palladium metal. However, they did not follow the time course of these processes, which is the reason why they failed in finding the intramolecular isomerization process during hydrogenation, and adopted both associative and dissociative mechanism in the same reaction simultaneously. Moreover, Gault and Ledoux chose the dissociative mechanism to elucidate the exchange and isomerization process of butene–D_2 reaction, although its rate was considerably faster than that of butene–C_3D_6 reaction (*19*). They explained this large difference in the rate by the increase of the active sites, which seems to be unrealistic from the following experimental result.

When the C_3H_6–C_3D_6–D_2 (5 : 5 : 1) reaction was conducted over Pd/SiO_2 at 190 K, deuterium addition and exchange reaction between C_3H_6 and D_2 proceeded simultaneously until all the deuterium was consumed to form propane (*27*). As the exchange reaction between C_3H_6 and C_3D_6 was negligibly slow at 190 K, it was necessary to raise the reaction temperature to follow the exchange process. These results strongly suggest that the large difference in the reaction rates between C_3H_6–D_2 and C_3H_6–C_3D_6 reaction is not due to the reconstruction of the surface structure as proposed by Gault *et al.* Instead the reaction mechanism changes as the concentration of adsorbed hydrogen varies. As seen in Figs. 3 and 5, the rate of C_3H_6–D_2 reaction was two orders of magnitude larger than that of C_3H_6–C_3D_6 reaction, and also the activation energy was considerably larger than that of the latter. These results clearly indicate that these reactions proceed with two different reaction mechanisms.

The main feature of C_3H_6–C_3D_6 reaction is as follows: (1) successive reaction, (2) no change of the isotope distribution at the initial stage of the reaction, (3) different activation energy for the exchange of each hydrogen. These results lead to the conclusion that this reaction proceeds with the dissociative mechanism including three independent intermediates; *n*-propenyl, sec-propenyl, and σ-allyl adsorbed species as illustrated in Figs. 9(a-1)–(a-3). Gault *et al.* (*18*) observed the double bond migration process through π-allylic intermediate (Fig. 9(a-4)) in the study of C_4H_8–C_3D_6 reaction at 273 K. At our experimental temperature, 240 K, this process was found to be slow, since we did not observe extensively exchanged propene in C_3H_6–C_3D_6 reaction.

Recently Rorris *et al.* (*14*) examined the hydrogenation of propene over highly dispersed Pd/SiO_2 catalysts (from 0.14 to 0.86 dispersion) in the temperature range of 228–192 K. They carried out their experiment in a differential flow reactor with $C_3H_6 : H_2/1 : 17$. When the large difference in hydrogen partial pressure (ca. 25 times) is taken into consideration, the observed turnover frequency and apparent activation energies in Fig. 5 correspond reasonably well to their results ($E_a = 7.7 + 0.8$ kcal mol^{-1}, turnover frequency = 0.2–0.3 at 201 K). The rate of hydrogenation measured by Rorris et al. is nearly proportional to the first power of the pressure of hydrogen. We found, however, that the rate of propene hydrogenation over Pd black was almost independent of the partial pressure of hydrogen (*27*). Kokes and Rennard reported similar results in ethene hydrogenation over palladium hydride (*28*). The difference between the data by Rorris *et al.* and ours may be explained by the difference in particle size of palladium metal employed, that is, the difference in the concentration of hydride in palladium metal (*22*).

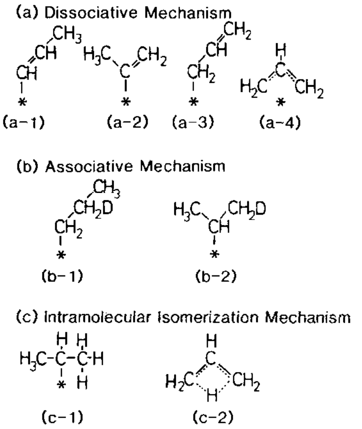


FIG. 9. Proposed reaction intermediates.

The reaction orders and activation energies were found to coincide with each other both for deuterium addition and exchange processes in C_3H_6–D_2 reaction. It is thus reasonable to consider that C_3H_6–D_2 reaction proceeds through common σ-alkyl intermediates (associative mechanism). Propane is formed by adding one more deuterium or hydrogen atom to *n*-propyl or sec-propyl adsorbed species as shown in Fig. 9(b). The monodeuteropropenes 3-d_1 and 1-d_1 are formed from sec-propyl species. If the methyl groups of sec-propyl species are equivalent for the abstraction of a hydrogen atom, the ratio of 3-d_1/1-d_1 must be equal to 3/2. The observed ratio extrapolated toward time zero was much smaller than this value and indicated that the adsorbed species were not symmetric.

If only the associative mechanism is operating, the relative ratio of the isotopic isomers should stay constant at the initial stage of the reaction, the ratio being determined by that of the reactivity between *n*-propyl and sec-propyl adsorbed species. A drastic change in the isotopic distribution for monodeuteropropene found in the present study indicates that there exists an additional intramolecular double bond migration process. The most plausible mechanism to explain for these phenomena is as follows: deuterium is first incorporated into propene molecule through σ-alkyl adsorbed state with the ratio of 0.88 (1-d_1) : 0.12 (2-d_1) for C_1 and C_2 carbons of the double bond, respectively, and then rapid intramolecular shift of C_3-hydrogen to C_1 position, with a resultant double bond migration, causes the decrease of 1-d_1 and the increase of 3-d_1 at the same time. The result of C_3H_5D–H_2 reaction strongly suggested this bond migration process.

Two kinds of reaction intermediates shown in Fig. 9(c) may be suggested for the intramolecular double bond migration process. The structure of (c-1) is the same as the sec-propyl species (b-2) in the associative mechanism, but they should be differentiated from each other. Otherwise the drastic change of the deuterium isotope distribution in Fig. 7 cannot be explained. Moreover, the σ-alkyl state (c-1) should be formed by some special surface hydrogen which is different from the adsorbed hydrogen equilibrated with the gas phase. The exchange reaction between them should be very slow, but in the absence of gaseous hydrogen, this type of surface hydrogen would be consumed quickly for the addition reaction and then the double bond migration does not proceed any more as shown by the broken lines in Fig. 8.

The other possible intermediate shown in Fig. 9(c-2) is similar to the one proposed by Smith and Swoap (*29*) and Gault and Touroude (*30*) for the intramolecular isomerization of olefin. Since this double bond migration did not proceed in the absence of hydrogen molecule (C_3H_6–C_3D_6 reaction), some structural change of the intermediate (c-2) should take place depending on the presence or absence of gaseous hydrogen. One possible explanation is as follows: in the absence of gaseous hydrogen, bridged hydrogen which shifts from methyl to methylene carbon tends to dissociate and forms allylic adsorbed species (a-4). The exchange and isomerization reaction through this allylic intermediate is very slow at these lower temperatures. In the presence of gaseous hydrogen, however, this dissociation step may be retarded by adsorbed hydrogen from the gas phase, which makes it possible that intramolecular double bond migration process takes place at lower temperatures.

There is no experimental evidence to determine which intermediate is appropriate, but the last intermediate seems to be more preferable because the activation energy for this process is the same as that for allylic type dissociative mechanism in C_3H_6–C_3D_6 reaction (7.0 kcal mol^{-1}).

CONCLUSIONS

(1) In the absence of hydrogen molecule in the gas phase, the exchange reaction of hydrogen in propene molecule proceeds via dissociative mechanism including *n*-propenyl, sec-propenyl, and σ-allyl adsorbed species. The activation energy for allylic intermediate is considerably different from propenyl type intermediate.

(2) In the presence of gaseous hydrogen, hydrogen addition and exchange reaction take place via associative mechanism involving *n*-propyl and sec-propyl adsorbed species. The latter species is not symmetric for hydrogen abstraction.

(3) When gaseous hydrogen is present, the intramolecular hydrogen scrambling takes place via additional mechanism of double bond migration.

ACKNOWLEDGMENTS

We should like to express sincere thanks to Professor Y. Morino for his encouragement throughout this work and to Mr. S. Mohara for his help in measuring mass spectra.

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