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Hydrogen Exchange Reactions between Olefins or an Olefin and Molecular Hydrogen over Alumina Studied by Microwave Spectroscopy

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The exchange reaction between propylene and deuterium was studied over alumina. The rate of the reaction was expressed by $V_{ex}=k[P_{D_2}]^{0.5}[P_{Pro}]^{0.0}$. In the initial stages of the reaction the *cis*- and *trans*-1-d_1 species of propylene were the only products of the exchange reaction, but the concentration of the 3-d_1 species increased continuously as the reaction progressed. The activation energy for the exchange reaction was about 8.2 kcal/mol.

Propylene-*cis*-d_1 was reacted over alumina, and the variation in the deuterium distribution of the propylene was followed by microwave spectroscopy. Isotope scrambling and "double-bond migration" occurred to considerable extents, while *cis-trans* equilibration between the two C_1 hydrogen positions proceeded even faster. In the reaction of propylene-3-d_1, the isotope mixing and "double-bond migration" were considerably slower than those of the *cis*-1-d_1 species. *Cis*- and *trans*-1-d_1 species were formed in equal amounts. The possible mechanism of these reactions is discussed on the basis of the results obtained.

n-Butene isomerization, especially double-bond migration, in the presence of perdeuteriopropylene over alumina was studied in a previous paper[1] in order to obtain further information about the reaction mechanism. It was concluded that the isomerization of *n*-butene, or at least the double-bond migration, occurs on some protonic sites formed on the catalyst by the adsorption of olefin molecules, and that extensive deuterium exchange during the isomerization proceeds independently of the isomerization.

In this report the exchange reaction between propylene and molecular deuterium was carried out over alumina to derive more information about the mechanism of the deuterium scrambling among terminal olefins, and to elucidate the nature of the catalytic action of the alumina.

Experimental

γ-Alumina employed in this study was obtained from Degussa Co., and was pretreated in the following manner. Dry oxygen was circulated over the catalyst at 600°C for two hours, and the catalyst was then cooled to 500°C, the oxygen was replaced by dry hydrogen, and the catalyst kept at this temperature for one hour. The system was then evacuated for two hours at 600°C. Usually 9 g of alumina was employed as the catalyst.

Propylene was obtained from Takachiho Shoji Co., and purified by repeated distillation *in vacuo*. The deuterium (Showa Denko Co.) had a quoted purity of 99.5 D%, and was used without further purification.

Methylacetylene from Takachiho Shoji Co. was treated several times with weakly alkaline deuterium oxide to re-

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[1] Y. Sakurai, T. Onishi, and K. Tamaru, submitted for publication in *Trans. Faraday Soc.*

place its acetylenic hydrogen with deuterium. Methylacetylene-1-d_1 thus obtained was selectively hydrogenated to propylene-*cis*-1-d_1 by a process similar to that developed by Rabinovitch and Looney.[2] Three samples of propylene-*cis*-1-d_1 were obtained and employed for the reaction. The deuterium contents were determined by mass spectrometry, and were found to be around 90% in all three cases. Microwave spectroscopic analysis of the samples revealed that they consisted of only the *cis*-1-d_1 and *trans*-1-d_1 species.

The 3-d_1 species of propylene was synthesized by reacting allyl chloride and deuterium oxide over zinc powder in an acetic anhydride medium. The deuterium content of the propylene-3-d_1 thus obtained was about 83%. According to the microwave spectroscopic analysis, the propylene-3-d_1 consisted solely of the 3-d_1 species without any trace of the other monodeuterated species.

A conventional closed circulating system with a total volume of about 300 cm³ was employed for the reaction. A mixture of propylene and deuterium was circulated over the alumina catalyst which was kept at a constant temperature (−21—60°C).

Analysis of the isotopic composition of the deuterium was carried out by gas chromatography using a $MnCl_2$-alumina column at liquid nitrogen temperature. The mass spectra of the propylene were recorded with an ionization, and the appropriate corrections were applied.

Microwave spectra of propylene and its mono-deuterated species were observed by Lide and Christensen,[4] and used for the quantitative determination of the deuterium contents at each hydrogen position of propylene-d_1 by Hirota and Morino.[5] Measurements were carried out at dry ice temperature with a conventional Stark modulation spectrometer. The $1_{01}-0_{00}$ transition was employed for the analysis, and the intensities of the neighboring peaks were compared. When the appropriate corrections were applied to the results,[5] the corrected intensity ratio was taken to show the relative abundance of the two species concerned.[6]

Results

Exchange Reaction between Propylene and Deuterium. The initial rate of the hydrogen exchange between propylene and deuterium was studied at propylene pressures between 11 and 44 cmHg, the partial pressure of deuterium being kept constant at 44 cmHg. The results are shown in Fig. 1. The initial rate of the hydrogen exchange was also studied at a constant pressure of propylene (22 cmHg), with a varying partial pressure of deuterium and the results are given in Fig. 2. The results of Figs. 1 and 2 show that proportional to square root of the deuterium pressure. This can be interpreted by postulating that the propylene is strongly adsorbed on the surface of alumina, and the deuterium molecules dissociate on the surface, to take part in the exchange reaction with the adsorbed propylene.

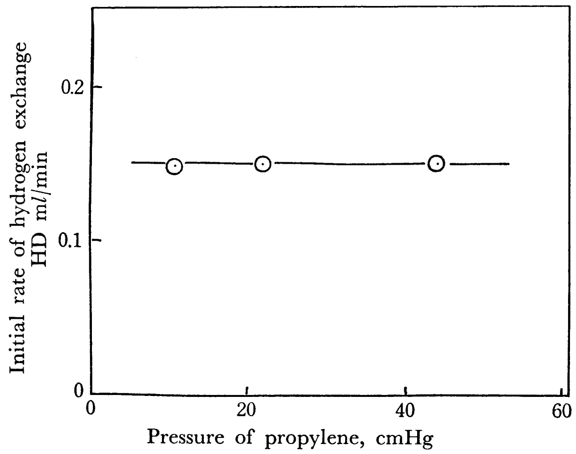

Fig. 1. Hydrogen exchange between propylene and deuterium over alumina. Dependence of the rate on partial pressure of propylene. $P_{D_2}=44$ cmHg.

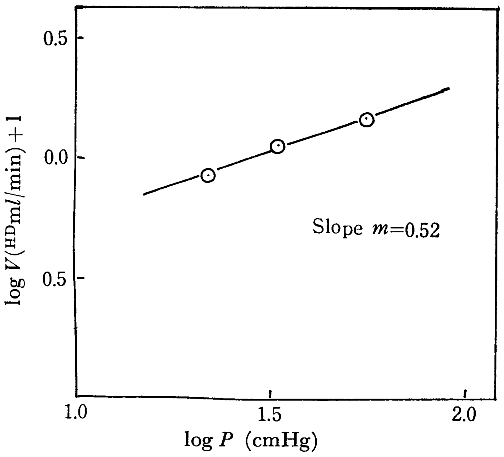

Fig. 2. Hydrogen exchange between propylene and deuterium over alumina. Dependence of the rate on partial pressure of deuterium. $P(C_3H_6)=22$ cmHg.

The hydrogen exchange between and equimolar mixture of propylene and deuterium was studied at temperatures between 0 and 60°C, and the Arrhenius plot of the exchange rate gave an activation energy of 8.2 kcal/mol. Recently deuterium exchange with hydrogen atoms in some olefins such as 1-butene, *cis*-2-butene and isobutene over alumina has been reported by Hightower and Hall.[7] They found an activation energy for the exchange reaction with D_2 of 5~6 kcal/mol, which is slightly smaller than the value of 8.2 kcal/mol obtained here for the reaction between propylene and deuterium.

As the reaction progressed, hydrogenation of the propylene was found to occur to a small extent, but its rate was always almost one order of magnitude smaller than that of the exchange reaction. Therefore, the hydrogenation of propylene may be neglected under these conditions, and the subsequent discussions will be entirely concerned with the exchange

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[2] B. S. Rabinovitch and F. S. Looney, *J. Amer. Chem. Soc.*, **75**, 2652 (1953).

[3] D. R. Herschbach and L. C. Kirisher, *J. Chem. Phys.*, **28**, 728 (1958).

[4] D. R. Lide, Jr. and D. Christensen, *ibid.*, **35**, 1374 (1961).

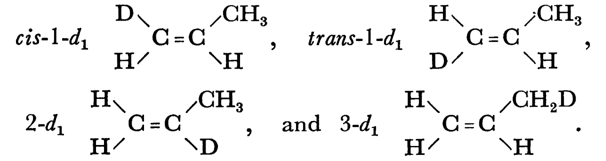
[5] Y. Morino and E. Hirota, *Nippon Kagaku Zasshi*, **85**, 535 (1964).

[6] E. Hirota, private communication: the observed intensity ratio should be divided by the following correction coefficient. *cis*-1-d_1/3a-d_1=1.0576, *trans*-1-d_1/3b-d_1=1.0488, and 2-d_1/3a-d_1=1.0990.

[7] J. W. Hightower and W. K. Hall, *J. Catal.*, **13**, 161 (1969).

reaction.

A mixture of propylene and deuterium (3 : 5) was reacted over alumina at three different temperatures (0, 24, and 56°C), and the resultant mono-deuterated propylene species were analyzed by microwave spectroscopy. Four mono-deuterated species are distinguishable either by their chemical properties or by microwave spectroscopy;



$$cis\text{-}1\text{-}d_1\ \ \overset{D}{\underset{H}{}}\!>C=C<\!\overset{CH_3}{\underset{H}{}},\qquad trans\text{-}1\text{-}d_1\ \ \overset{H}{\underset{D}{}}\!>C=C<\!\overset{CH_3}{\underset{H}{}},$$

$$2\text{-}d_1\ \ \overset{H}{\underset{H}{}}\!>C=C<\!\overset{CH_3}{\underset{D}{}},\quad \text{and}\quad 3\text{-}d_1\ \ \overset{H}{\underset{H}{}}\!>C=C<\!\overset{CH_2D}{\underset{H}{}}.$$

The fractions of the four mono-deuterated species were plotted against the number of deuterium atoms which entered the propylene by the exchange reaction. The results are shown in Fig. 3. The total concentrations of the mono-deuterated species were always normalized to 100%. The notable features of the results in Fig. 3 are: i) The amount of the 2-*d* species formed in the reaction was negligible. A small amount of 2-d_1 species was observed after prolonged reactions, but its concentration was at most 4—5% of the total mono-deuterated propylene. ii) The *cis*-1-d_1 and *trans*-1-d_1 species were formed in approximately equal amounts throughout the course of the reaction. iii) The fraction of the 3-d_1 species increased continuously as the reaction proceeded, but its contribution was almost zero in the very initial stages of the reaction. In other words, *cis*-1-d_1 and *trans*-1-d_1 propylene were the only mono-deuterated species produced in the early stages of the exchange reaction. iv) At high conversion levels the deuterium in the propylene was equally distributed among the five hydrogen positions at C_1 and C_3. v) Reaction at the three different temperatures gave rise to similar deuterium distributions, which meant that the activation energy for the deuterium shift to form the 3-d_1 species ("double-bond migration") was nearly equal to that of the exchange reaction, 8.2 kcal/mol.

Hydrogen Exchange Reactions between Deuterated Olefins. When propylene-*cis*-1-d_1 was circulated over alumina at 30°C, isotope scrambling resulting in $C_3H_4D_2$ and $C_3H_3D_3$ occurred rapidly as shown in Fig. 4. Microwave spectroscopic analysis of the mono-deuterated propylene revealed that the deuterium which had initially been mainly at the C_1 *cis* position moved rapidly to the other positions on the C_1 and C_3 atoms, and attained an equilibrium distribution within one hour (Fig. 5). As Fig. 4 shows, the relative concentrations of the four isotopic propylene species, *i.e.*, C_3H_6, C_3H_5D, $C_3H_4D_2$, and $C_3H_3D_3$, which were detected in the course of the reaction, became constant after a reaction time of about one hour. These results suggest that the shift of the deuterium to yield the 3-d_1 species ("double-bond migration") is an intermolecular process.

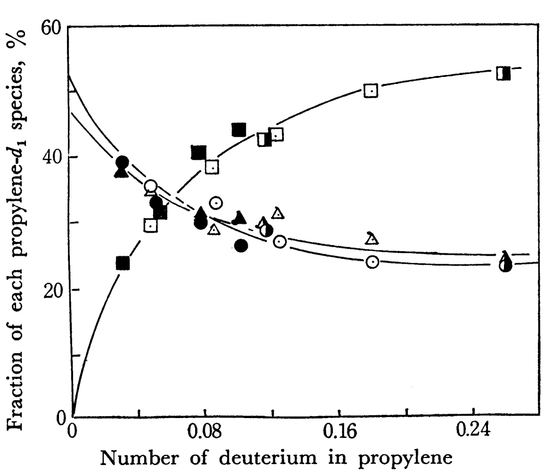


Fig. 3. Temperature dependence of deuterium distribution in propylene.
●▲■: 0°C, ○△□: 24°C, ◐◭◧: 56°C.

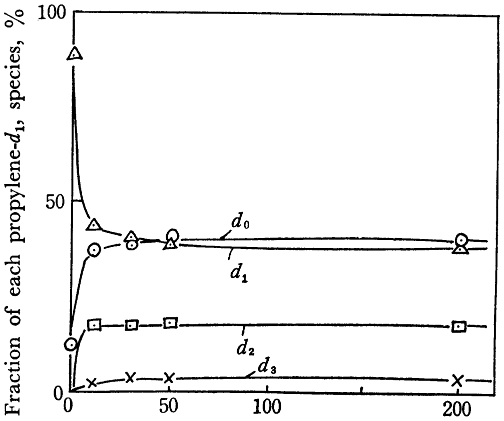


Fig. 4. Isotope mixing among the propylene, the change in deuterium content in propylene over alumina at 30°C.
○: C_3H_6, △: C_3H_5D, □: $C_3H_4D_2$, ×: $C_3H_3D_3$

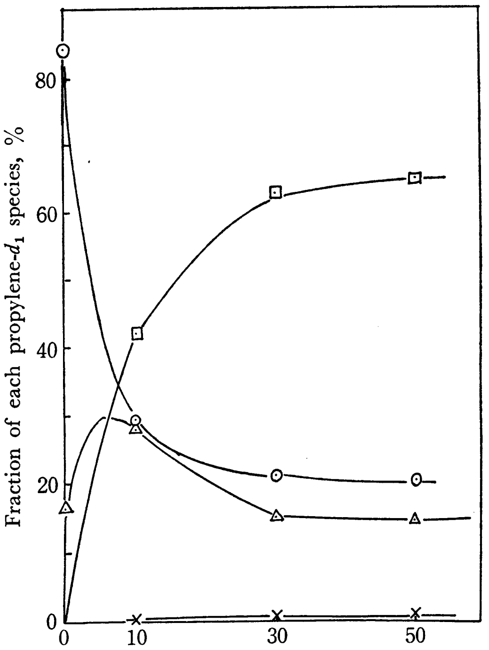


Fig. 5. Position of propylene-d_1 over alumina at 30°C.
□: 3-d_1, ○: *cis*-1-d_1, △: *trans*-1-d_1, ×: 2-d_1

When the reaction temperature was lowered, it was clearly demonstrated that *cis-trans* equilibration between the two hydrogen positions at C_1 atom occurred much more rapidly than "double-bond migration" to yield the 3-d_1 species. The activation energy for the *cis-trans* equilibration is lower than the "double-bond migration." The results are given in Fig. 6. Fig. 6 is for reaction at −21°C using sample B of the propylene-*cis*-1-d_1. The rate of isotope mixing to form $C_3H_4D_2$ and $C_3H_3D_3$ was considerably reduced at these temperatures.

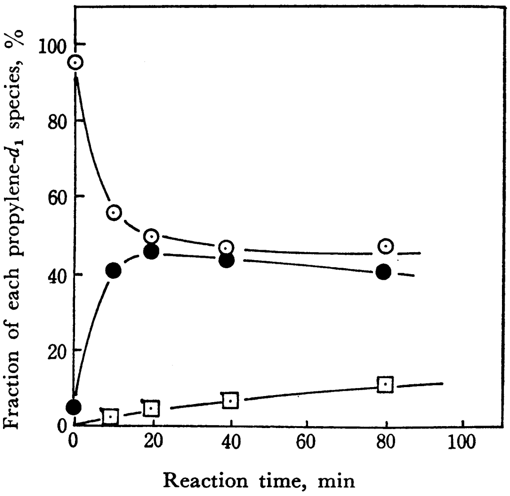


Fig. 6. The change in deuterated position of propylene-d_1 over alumina at −21°C.
○: *cis*-1-d_1, ●: *trans*-1-d_1, □: 3-d_1

When the 3-d_1 species of propylene was circulated over alumina at 0°C. under the similar conditions, *cis*-1-d_1 and *trans*-1-d_1 species formed in exactly equal amounts as shown in Fig. 7. The rate of the formation of the 1-d_1 species, however, was considerably slower than the rate of formation of the 3-d_1 species from *cis*-1-d_1 propylene.

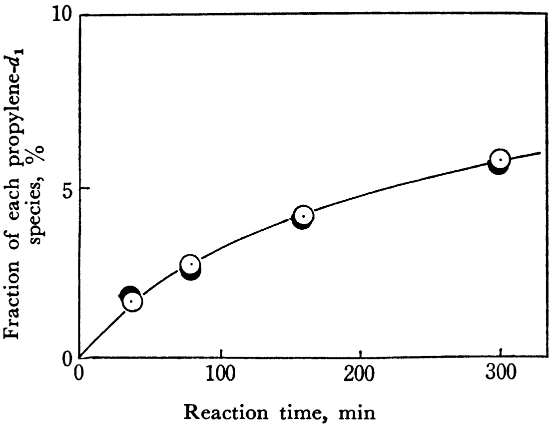


Fig. 7. Reaction of propylene-3-d_1 over alumina at 0°C.
○: *cis*-1-d_1, ●: *trans*-1-d_1

Discussion

Three kinds of the reactions were involved in the experiments described above. The first is the exchange reaction between propylene and deuterium molecule. The second is isotope mixing among the propylene isomers, and the third is *cis-trans* equilibration of the deuterium in the two hydrogen positions on the C_1 atom.

The first reaction can be considered to proceed *via* the interaction of adsorbed propylene and a deuterium atom formed by dissociation of deuterium on the surface. This view is supported by the observed rate equation for the exchange, $V_{ex}=k[P_{D_2}]^{0.5}[P_{Pro}]^{0.0}$. The adsorption of propylene over alumina appears to be dissociative at C_1 position, because the deuterium exchange occurred selectively in the hydrogen positions at C_1 atom. If an associative mechanism is involved, where deuterium adds to the adsorbed propylene to form an isopropyl (or propyl) intermediate, then substantial amounts of the 3-d_1 (or 2-d_1) species should appear even in the initial stages of the reaction. This was not found in the experiments. Thus, propylene can be assumed to adsorb on alumina dissociatively rather than associatively.

The second reaction may correspond to the double-bond migration of *n*-butene over alumina described previously.[1] Isotope mixing among the propylene isomers as shown in Fig. 4 and "double-bond migration" in the mono-deuterated species as shown in Fig. 5 occurred at a comparable rate and both reactions get to final distribution in half an hour at 30°C. At lower temperatures such as −21°C the rates of both reactions were considerably slower. This suggests the hydrogen dissociation at C_3 and its association at C_1 position. Isotope mixing thus accompanies "double-bond migration."

The third reaction, the *cis-trans* equilibration of deuterium in the two hydrogen positions on the C_1 atom occurred very rapidly even at temperatures as low as −21°C. At −21°C the isotope mixing and "double-bond migration" slowed down remarkably. This suggests that the *cis-trans* equilibration reaction which may correspond to the *cis-trans* isomerization of 2-butene proceeds intramolecularly and is probably independent of the above two reaction. Hightower and Hall[8] studied that reaction of a mixture of butene and perdeuterio-butene over alumina, and concluded that *cis-trans* isomerization occurred by an intramolecular rearrangement.

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[8] J. W. Hightower and W. K. Hall, *J. Amer. Chem. Soc.*, **89**, 778 (1967).