A Kinetic Study of the Catalytic Isotopic Hydrogen Exchange of Propene with Deuterium Oxide on Palladium Black

By Yoshie HIRONAKA and Kozo HIROTA

(Received May 16, 1965)

It has already been reported[1,2] that methyl hydrogen is, of all the hydrogen atoms in propene, the most exchangeable on palladium black, while methine hydrogen is the most exchangeable on nickel judging from the subspecies-distribution of propene-d_1 in the product.

On the other hand, when the kinetic study of this reaction was carried out on nickel, it was concluded that the exchange of vinyl hydrogen attained equilibrium faster than that of methyl hydrogen.[3]

Since the mechanism of the reaction has been discussed in the case of palladium black only in terms of the subspecies-distribution of d_1,[1,2] information concerning the mechanism has been insufficiently detailed for us to reach a final conclusion. The present work was therefore undertaken in order to confirm kinetically the mechanism of the isotopic hydrogen exchange of propene with deuterium black.

Experimental

Materials.—Propene obtained from the Takachiho Industrial Co. (purity: 99.7%) was used without any further purification. Deuterium oxide obtained from the Showa Denko K. K. (the deuterium content, 99.7%) was used also without any further purification. The palladium black used as a catalyst, obtained from the Mitsuwa Kagaku Yakuhin K. K., was reduced at 180°C with hydrogen which had been purified by diffusion through a palladium tube, until no water was produced, followed by degassing for at least four hours at the same temperature.

Procedure.—Propene and deuterium oxide were throughly outgassed and were charged in vacuo at the temperature of liquid nitrogen in an ampoule (200 cc.) in which the catalyst had already been prepared. The ampoule was kept at reaction temperature. In order to carry out a kinetic run, about one milliliter (corresponding to 0.5% in a reactor) of gas was sampled from the ampoule at each reaction time. The gas was subjected to mass spectrometric analysis in order to determine the d_y-distribution (Hitachi RMU-5B). The infrared method was also applied to the qualitative analysis of the product in order to study the activation energy of exchange for each hydrogen atom in propene.

Results

The Kinetics of the Reaction.—Table I shows the d_y-distribution obtained at various times at 50°C, d_y representing the percentage of the isotopic species containing y deuterium atoms at time t, while ϕ is defined by Eq. 1:

$$\phi=\sum_{y=1}^{6} y d_y \qquad (1)$$

The exchange rate constants measured at 50°C were calculated by assuming the reaction to be first order with respect to the concentration of propene (d_0). They are shown in Table I. The triangles in Fig. 1 show the plots of the log ($d_{0t}-d_{0\infty}$) vs. the time (curve a), while the circles show the plots of the log ($\phi_\infty-\phi$) vs. the time (curve b), with the equilibrium value of ϕ denoted by ϕ_∞. Both plots show approximately straight lines. Such a tendency was not found in nickel.[3]

---

[1] K. Hirota, Y. Hironaka and E. Hirota, *Tetrahedron Letters*, **1964**, 1945.

[2] K. Hirota and Y. Hironaka, *J. Catalysis*, **4**, No. 5 (1965).

[3] K. Hirota and Y. Hironaka, This Bulletin, **37**, 535 (1964).

TABLE I. d_y-DISTRIBUTION IN KINETIC STUDY

No.	Time, hr.	d_0	d_1	d_2	d_3	d_4	d_5	d_6	ϕ%
1	0.25	84.3	14.4	1.3	—	—	—	—	16.0
2	0.75	66.9	27.6	5.0	0.5	—	—	—	38.6
3	2.0	41.7	39.2	15.7	3.1	0.3	—	—	81.1
4	3.5	27.0	40.2	24.0	7.6	1.2	—	—	115.8
6	7.5	11.0	29.5	33.0	19.3	6.3	0.9	—	183.1
8	13.0	4.0	18.3	32.5	28.7	13.5	3.0	—	238.4
9	17.0	2.6	13.4	29.4	30.3	18.3	5.2	0.7	267.2
10	23.0	1.8	9.7	24.6	31.9	22.9	8.2	1.2	294.4

Pd: 3.26 g. C_3H_6: 7.26 mmol. D_2O: 29.5 mmol. Temp.: 50°C.

TABLE II. THE TEMPERATURE DEPENDENCY OF THE REACTION RATE

No.	Temp., °C	Time, hr.	d_0	d_1	d_2	d_3	d_4	ϕ	k, hr^{-1}
4227	50	5.5	29.7	39.8	22.7	6.6	1.2	109.8	20.0
4308	55	4.0	32.1	40.8	20.9	5.4	0.8	102.0	28.6
4311	60	3.0	34.0	40.4	19.7	5.0	0.9	98.3	42.9

Catalyst: 3.26 g. C_3H_6: 7.26 mmol. D_2O: 30 mmol.

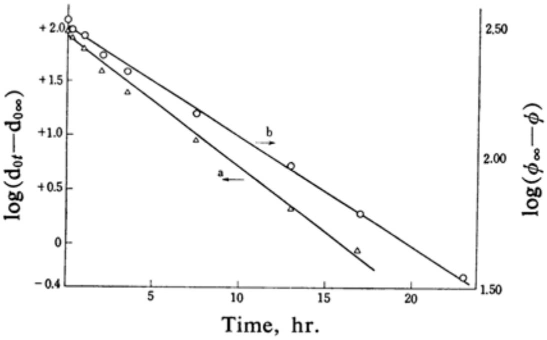


Fig. 1. The plots of $\log(d_{0t}-d_{0\infty})$ vs. time (△) and $\log(\phi_\infty-\phi)$ vs. time (○).

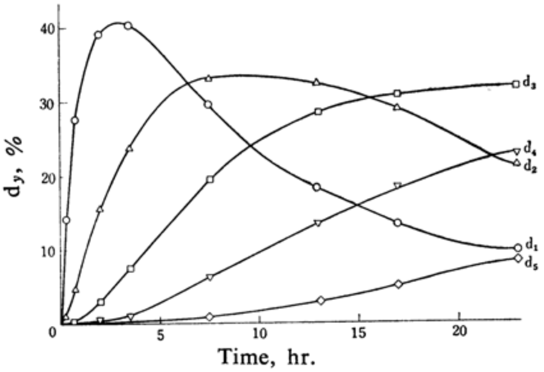


Fig. 2. Time dependency of d_y-species.

The time-dependency of the d_1—d_5 species produced (%) is shown in Fig. 2, with $\sum d_y = 100\%$. Both d_1 and d_2 rose to a maximum and then decreased, while the others increased for 23 hr.

Activation Energy.—The exchange was carried out at 55 and 60°C, as well as at 50°C, on the same palladium black, which was reduced with purified hydrogen gas prior to each run. When the activity was checked in the final run under the same conditions as in the initial run, the two examinations agreed well.

The d_y and ϕ values, as well as the k values, are summarized in Table II.

The apparent activation energy obtained from the first order rate constant, k, was 9 kcal./mol. The infrared spectra of three runs are practically identical over the range of the C-D stretching region (2100—2300 cm^{-1}).

Discussion

From the data obtained by microwave analysis,[1] methyl hydrogen of propene was the most exchangeable of the three kinds of hydrogens atoms at the initial stage of the reaction (3-d_1=59.1%, 2-d_1=14.1%, t-1-d_1=13.1%, c-1-d_1=13.7%[1]*)

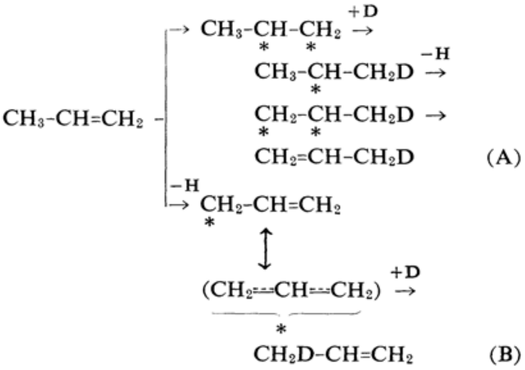
Nevertheless, there still remains a question whether or not the exchange occurred according to the mechanism concluded from the analysis of the subspecies-distribution of d_1 in the reaction process. This question can be solved by measuring the rate of this reaction. Crawford and Kemball[4] suggested that the $\log(\phi_\infty-\phi)$ curve was composed of two or more straight lines if the molecule has two or more kinds of hydrogen atoms different in their exchangeabilities. In the present case, since the $\log(\phi_\infty-\phi)$ vs. time plot shows a straight line in Fig. 1, the exchange rate of

---

* This data is shown in Ref. 1.

[4] E. Crawford and C. Kemball, *Trans. Faraday Soc.*, **58**, 2452 (1962).

all the hydrogen atoms in propene may be equal, regardless of the groups to which they belong. However, for the purposes of explaining the finding that 3-d_1 is most abundant in the subspecies-distribution of d_1, it seems convenient to say that there are two different paths of methyl hydrogen exchange;



i. e., double-bond migration (A) and the dissociative adsorption of methyl hydrogen (B), the former isomeric mechanism having already been proposed.³⁾

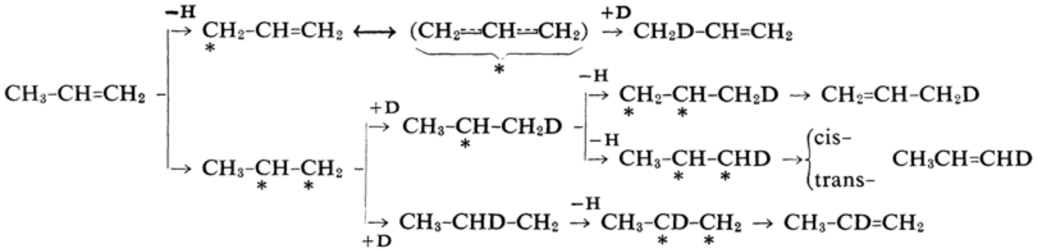
If the rate-determining step of the exchange is the adsorption of propene, the activation energies would be different between the A and B mechanisms, while the activation energy for methyl and methylene hydrogen exchange would be equal as they passed through the A reaction process. Secondly, if some other step is the rate-determining step, the activation energies of A and B would not be very different in general. The activation energy as determined by means of the rate constant, about 9 kcal./mol., would be the same with respect to the six hydrogen atoms in propene, because the infrared spectra of all three runs are practically identical, as has been mentioned above, as are their d_y-distributions (Table II).

The activation energy observed on palladium black is smaller than the value (13.7 kcal./mol.) obtained by Twigg,⁵⁾ who studied the exchange between deuterium gas and propene on nickel catalyst. The above value, however, is reasonable, because palladium is generally known to be more active than nickel in the catalytic hydrogenation of ethylene. On the other hand, the activation energies were 21.4 kcal./mol. and 23.7 kcal./mol. in the isotopic hydrogen exchanges of ethane⁶⁾ and propane⁷⁾ respectively with deuterium gas on evaporated palladium film.

Considering these facts, a higher activation energy seems to be required for the exchange of the hydrogen atom of saturated hydrocarbon. Nevertheless, for the exchange of methyl hydrogen in propene the activation energy is given as only 9 kcal./mol. If we assume the mechanism of methyl hydrogen exchange in propene is likely to be similar to that of ethane or propane, the activation energy would be higher. Considering that the existence of the dissociated propene on palladium black as an allyl-type intermediate ($CH_2{=\!=}CH{=\!=}CH_2$) is highly probable, as has been mentioned already,²⁾ the activation energy for the methyl exchange of propene would become smaller than that of propane or ethane, because the allyl-type intermediate is more stable than a propyl or ethyl intermediate. Though the rate-determining step could not be determined in this study, it may be considered that methyl exchange occurs according to both mechanisms, A and B, the exchange rates of which are given as nearly equal on the basis of the subspecies-distribution of d_1 and of kinetic studies.

Accordingly, the reaction scheme would be shown in Scheme 1.

On the other hand, it is possible that the exchange occurs according to either a multiple or a step-by-step mechanism⁸⁾ when the d_2-species are produced. Morino and Hirota⁹⁾ calculated the subspecies-distribution of d_2 using a statistical method. Their calculated values



Scheme 1

---

5) G. H. Twigg, ibid., **35**, 934 (1939).

6) J. R. Anderson and C. Kemball, *Proc. Roy. Soc.*, **A233**, 361 (1954).

7) F. G. Gault and C. Kemball, *Trans. Faraday Soc.*, **57**, 1771 (1961).

8) Cf. G. C. Bond, "Catalysis by Metals," Academic Press, London and New York (1962), p. 191.

9) Y. Morino and E. Hirota, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **85**, 535 (1964).

agreed well with the observed values. However, it was still impossible to determine which of the two mechanisms is the more probable.

If the exchange occurred according to the multiple process, highly-deuterated species would appear, even at the initial stage of reaction. If, on the other hand, the exchange occurred step-by-step, highly deuterated species would not exist at the initial stage of reaction. Therefore, the step-by-step mechanism may be more suitable in this reaction, because highly-deuterated species do not appear at the initial stage of reaction, as is shown in Table I; moreover, the amounts of d_1 and d_2 species rose to maxima and then decreased as Fig. 2 shows.

It was found to be obviously unreasonable to rely only on the d_y-distribution in determining the mechanism of reaction, because even if the d_y-distribution is the same between two different samples, subspecies-distributions of d_y are not always the same as has been pointed out in a previous paper.1) For instance, d_y-distributions of propene at the initial stage of exchange reaction were nearly the same on palladium and on nickel, even though the subspecies-distributions of d_1 were clearly different.

Summary

A reaction mechanism for the catalytic isotopic hydrogen exchange of propene with deuterium oxide on palladium has been offered on the basis of the observed reaction rate and activation energy.

It has been concluded from the observed similarity in the d_y-distribution and infrared spectra of the products at different temperatures that the exchange rates of the six hydrogen atoms in propene are nearly equal, while their activation energies are all 9 kcal./mol.

The exchange of methyl hydrogen atoms has been estimated to occur according to the double-bond migration mechanism as well as the dissociation mechanism.

A difference in catalytic activity has been found between palladium and nickel, even when their d_y-distributions are nearly the same.

Chemistry Department
Faculty of Science
Osaka University
*Nakanoshima, Osaka**

---

* New address since July, 1965: Kitatoneyama, Toyonaka, Osaka.