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AN INFORMATION ON THE PECULIAR CHEMISORBED STATE OF PROPENE ON PLATINUM

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In the previous reports on nickel and palladium catalysts (1), the chemisorbed states of propene were investigated, based upon the subspecies-distributions of propene-d_1 in the product of the exchange reaction and hydrogenation with deuterium and deuterium oxide:

$$C_3H_6 + \chi D_2 \longrightarrow C_3H_{8-y}D_y , \quad C_3H_{6-z}D_z , \quad (1)$$

$$C_3H_6 + zD_2O \longrightarrow C_3H_{6-z}D_z , \quad (2)$$

and it was concluded that both reactions occur via the half-hydrogenated state, C_3H_7, so far as nickel and palladium are concerned.

Similar investigation was extended on platinum catalyst by the static method under the similar condition as that of nickel and palladium, as shown in Table I, where the distributions of deuterium in the remaining propene are described.

TABLE I. Experimental Conditions and Deuterium-distribution of Reaction Products.

(A) Experimental condition

			Sample (mole)				Reaction	
No.	Catalyst	g	C_3H_6	D_2O	D_2	C_3H_6/D_2	Temp.	Time
5505	Pt-black	0.50	2.18	–	1.09	2.0	20°C	20 min.
41017	Pt-black	0.30	2.18	9.9	–	–	25°C	100 hr.

(B) Distribution of deuterium in remaining propene (%)

No.	d_0	d_1	d_2	d_3	d_4	d_5	d_6	$\psi = \frac{1}{6}\sum j d_j$
5505	60.6	21.9	9.5	4.7	2.6	0.7	–	11.5
41017	53.5	26.9	8.9	4.9	2.7	1.9	1.2	14.7

TABLE II. Distribution of Subspecies (%) of Propene-d_1 *)

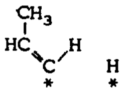
No. of Run Subspecies	5505 Pt, D_2	41017 Pt, D_2O	3513**) Ni, D_2O	3515**) Pd, D_2O
$CH_2D\text{-}CH{=}CH_2$	21.1 ± 1.7 (7.0)	19.5 ± 2.1 (6.5)	22.5 ± 2.7 (7.5)	59.2 ± 2.2 (19.7)
t-$CH_3\text{-}CH{=}CHD$	39.1 ± 3.3	47.4 ± 4.8	9.5 ± 2.1	13.1 ± 1.3
c-$CH_3\text{-}CH{=}CHD$	13.1 ± 2.5	5.8 ± 1.4	9.9 ± 2.2	13.7 ± 1.5
$CH_3\text{-}CD{=}CH_2$	26.7 ± 3.6	27.3 ± 4.5	58.1 ± 5.1	14.1 ± 1.3

*) Trans- and cis- form denotes the position of deuterium against the CH_3 group.

**) These two runs, reported already, were shown again for the sake of comparison.

Table II shows subspecies-distribution of propene-d_1 determined by the microwave-spectroscopic method. As in the cases of nickel and palladium, the distribution is found almost the same for two samples, for which the deuterium sources are deuterium gas and deuterium oxide, respectively. On the other hand, much difference is obtained in exchangeability of the two hydrogen atoms of the methylene group. Actually the trans hydrogen is the most exchangeable among the six hydrogen atoms. A considerable amount of exchange occurs also at the methine position.

These findings suggest that, besides the associative state $CH_3\underset{*}{C}H\underset{*}{C}H_2$ assumed in the previous papers, there is some additional state which may bear a steric effect of the methyl group to favor the exchange at the trans position. A qualitative observation of the distribution of C_3H_6-d_2's also indicates the existence of a state not observed in the cases of nickel and palladium. As the state, a dissociative one I, proposed already (2,3), would be plausible.



(I)

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Reference

1. K. Hirota, Y. Hironaka and E. Hirota, Tetrahedron Letters, p.1645 (1964); J. Catalysis, **4**, 602 (1965).
2. A. Farkas and L. Farkas, J. Am. Chem. Soc., **60**, 22 (1938).
3. R. L. Burwell, Jr., Chem. Rev., **57**, 895 (1957).