

DIFFERENCE OF THE CATALYTIC ACTIVITY BETWEEN NICKEL AND
PALLADIUM IN THE ISOTOPIC HYDROGEN EXCHANGE OF PROPENE WITH
DEUTERIUM OXIDE

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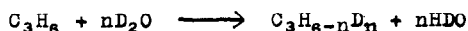
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In connection with the mechanism of olefin hydrogenation,
catalytic hydrogen exchange of propene with deuterium oxide(A)



has been investigated at room temperature by the quantitative analysis of the deuterated products, as adopted in the similar reaction of paraxylene (1). Propene includes, however, three kinds of hydrogen-carbon bonding, CH, CH₂ and CH₃, so that application of the infrared absorption and nuclear magnetic resonance methods was found to be insufficient to assign the detailed position of deuterium substitution. This difficulty of analysis was overcome by utilizing the microwave absorption spectroscopic method. Since this attempt has been found very effective, the result on nickel and palladium will be communicated.

Experimental procedure was the same as in the paper now

in press (2). The microwave absorption spectrometer equipped in Morino's Laboratory, Faculty of Science, The University of Tokyo, was used. Besides, the distribution of deuterated propenes $C_3H_{6-n}D_n$ ($=d_n$) in the product was determined by the mass spectrometer hitherto used.

Experimental condition of the runs carried out on nickel and palladium was selected so that their average deuterium concentration ψ was nearly equal each other. Table I shows that both samples indicate similar d_n -distribution. However, the distribution of d_1 among subspecies was found quite different as shown in Table II. by the use of microwave spectroscopy. Principle of the analysis is described in the appendix.

By this result the differences of catalytic activity between nickel and palladium are evidently shown; i.e., (a) methine hydrogens become the most exchangeable on nickel, (b) methyl hydrogen is slightly more exchangeable than methylene and methine hydrogens on palladium, and (c) the exchangeability of two hydrogens at the methylene group is the same, irrespective to trans- or cis-position to the methyl group. Such findings^{*)} would suggest the adsorbed state of propene on both catalysts to be discussed in future.

The qualitative result on the distribution of d_2 gave us also an interesting conclusion as if the first and second deuterium exchange occur independently. This finding teaches us for the deuteration to proceed successively, suggesting that the exchange occurs more slowly in comparison with the

*) By use of NMR and IR methods, findings (a) and (b) was estimated, though qualitatively, by us (unpublished).

life of adsorption, even if the double bond be opened during adsorption of propene on metals as usually assumed.

We express our sincere thanks to Professor Yonezo Morino who taught us the application of microwave spectroscopy to the present research.

TABLE I
Distribution of Products among $C_3H_{6-n}D_n (=d_n)$ *)

Catalysts (g)	Temp. °C	Time hr	Deuterium distribution					Ψ **)
			d_0	d_1	d_2	d_3	d_4	
Ni 1.65	17	25	58.4	33.3	7.3	1.0	—	8.5
Pd 0.50	25	150	51.3	36.8	10.7	1.6	—	10.4

*) Initial amount : $C_3H_6 = 2.18$ m mole; $D_2O = 10$ m mole.

**) $\Psi = \left(\frac{1}{6}\right) \sum_{n=1}^6 nd_n$

TABLE II
Distribution of d, among Subspecies

Catalyst	$CH_2DCH=CH_2$	$CH_3-CD=CH_2$	cis-	trans-
			$CH_3-CH=CHD$	$CH_3-CH=CHD$
Pd	$59.2 \pm 2.1 (19.4)^*$	14.1 ± 1.3	13.7 ± 1.5	13.1 ± 1.3
Ni	$22.5 \pm 2.7 (7.7)$	58.1 ± 5.1	9.9 ± 2.2	9.5 ± 2.1

*) Numerals in parenthesis denote the percentage allotted to one H atom.

Appendix

The microwave spectrum of propylene and its isotopic species was investigated in detail by Lide et al. (3, 4), who determined the molecular structure, dipole moment, and the potential barrier hindering the methyl rotation. The propylene molecule is a near-prolate symmetric rotor and shows only four rotational transitions strong enough to observe in the cm wave region. The present report is primarily concerned with the abundance of the isotopic species, which may be determined by comparing the intensities of the $0_{00} - 1_{01}$ transitions of the various species. Recently a technique of measuring the relative intensities of the microwave lines was developed by Esbitt and Wilson (5), and necessary equipments are available in Morino's laboratory (6). Details of the analysis will be published elsewhere.

Reference

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