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Application of Microwave Spectroscopy to the Isotopic Analysis of the Reaction Products of Methylacetylene with Deuterium on Nickel Catalysts

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The reaction of methylacetylene with deuterium was investigated in a static system over nickel powders at 25°C, and the products were analyzed by the mass spectroscopic and microwave spectroscopic methods. The propylene yield in the products was ca. 0.8, similar to the result presented in the literature. In sharp contrast with the reaction of propylene with deuterium, the methyl positions of propylene could not be deuterated, suggesting that the double-bond migration does not occur during the reaction. Of all the propylene-d_2, *cis*-dideuteropropylene consisted of more than half the product at the 70% conversion. Protium concentration on the surface was estimated to be very low during the reaction. This is in contrast to the situation in the reaction of olefins with deuterium.

INTRODUCTION

In order to investigate the mechanism of hydrogen addition to the carbon–carbon triple bond, methylacetylene is a suitable compound rather than acetylene, because of the different character of its three carbons. Nevertheless, very few studies have been made on this reaction, much fewer when deuterium tracer is used (*1*). From the mechanistic viewpoint of studying reactions, it is interesting to analyze quantitatively the isotopic isomers in the reaction products (*2*). Application of the microwave spectroscopy, therefore, is attempted to the reaction (1) of methylacetylene with deuterium on nickel catalysts, because this new method was found very useful for the isotopic analysis (*3*).

$$C_3H_4 \xrightarrow{+D_2} C_3H_{6-x}D_x \xrightarrow{+D_2} C_3H_{8-y}D_y, \quad (1)$$
$$(x = 0, 1, 2, \ldots, 6;\ y = 0, 1, 2, \ldots, 8).$$

If propane be thus produced via propylene, distribution of the isotopic isomers of propylene would be the same as that of the reaction of propylene with deuterium. However, both distributions are found to be different in several points from the conclusion obtainable by simple reasoning. These interesting findings are reported, therefore, with special regard to the difference between acetylene and methylacetylene.

EXPERIMENTAL METHODS

Materials. (a) Nickel powders were prepared by decomposition of nickel formate in the reaction tube kept at 350°C. The amount of initial nickel formate was equivalent to 0.1 g of metallic nickel. (b) Methylacetylene of 95.0% of purity (Takachiho Chem. Ind. Co., Tokyo) was purified by freezing out of the carrier gas stream on elution from the gas chromatograph in which a 1-m column of dimethyl *sulforane* was charged and was operated at the room temperature. (c) Deuterium of 99.5% purity (Takachiho Chem. Ind. Co., Tokyo) was used without purification.

Apparatus and procedure. The reaction was carried out by a static system in a glass tube (300 ml), which was equipped with a mercury manometer and contained catalyst powders. The catalyst was treated with 200 mm of protium at 300°C for 24 hr before each experiment, followed by degassing for 2 hr at the same temperature, and was cooled down to the reaction temperature (25°C). Then, the reaction mixture consisting of methylacetylene and deuterium was introduced into the reaction tube kept at 25°C.

When a desired degree of hydrogenation was reached, the produced hydrocarbons were taken out and freed of hydrogen by pumping through a spiral trap cooled in liquid nitrogen. They were separated by gas chromatography into methylacetylene, propylene and propane, so as to be subjected to mass spectroscopic and microwave spectroscopic analyses. The apparatuses used in both measurements were installed at Osaka University and Sagami Central Chemical Institute, respectively.

RESULTS

Reaction curve and selectivity. A typical curve with a reaction mixture which is consisted of methylacetylene (29.8 mm) and protium (59.7 mm) is shown against time (min) in Fig. 1. The acceleration point (A) appears at the total pressure decrease of about 34 mm. Finally, total pressure falls down to 30.5 mm and remains constant. This pressure can be expected to be final if the hydrogenation $C_3H_4 + 2H_2 \rightarrow C_3H_8$ proceeds stoichiometrically, so that any polymerization process may be neglected in the present reaction conditions.

Selectivity, defined by P (propylene)/ [P (propylene) + P (propane)], was 0.78 (No. 2) in the reaction of standard mixture ($C_3H_4:D_2 = 1:2$). This value may be reasonable, judging from the results of Mann and Khulbe (*4*), who obtained 0.85 at 75°C and 0.88 at 122°C. The fact that propylene is the major product is favorable to the present research where discussion is focused on the production of propylene.

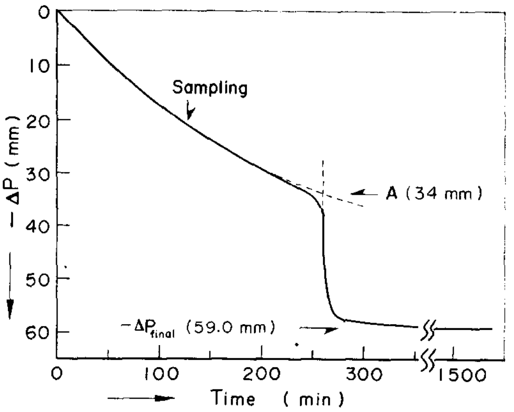


FIG. 1. Typical pressure decrease, $-\Delta P$, against time curve for the hydrogenation of methylacetylene on nickel at 25°C; $(P_{C_3H_4})^0 = 29.8$ mm, $(P_{H_2})^0 = 59.7$ mm.

"Fine" and "hyperfine" deuterium distribution. The percentage distribution of the various deuteropropylenes formed by the reaction of methylacetylene with deuterium was determined mass spectrometrically. The distribution of isotopic isomers of mono- and dideuteropropylene was determined by the microwave spectroscopy. These two kinds of deuterium distribution were nomenclatured as "fine" and "hyperfine" distribution, respectively, as proposed already (*5*).

Fine distributions of deuteropropylenes are described in Table 1, while hyperfine distributions of mono- and dideuteropropylenes in Table 2, where the percentage of four isomers are described, because other possible three isomers of dideuteropropylene could not be detected.

Table 1 indicates that the fine distribution is constant during the reaction, at least until 70% conversion (No. 2) which is defined as the percentage of the total pressure decrease to the initial partial pressure of methylacetylene. Nevertheless, the degree of deuterium-exchange in methylacetylene was very small even at the 70% conversion (No. 2); i.e., fine deuterium distribution of methyacetylene is

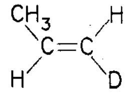
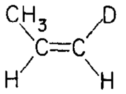
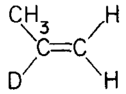
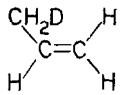
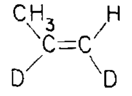
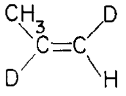
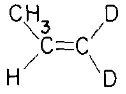
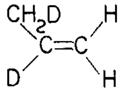
TABLE 1
"FINE" DISTRIBUTION OF DEUTEROPROPYLENES AT 25°C ON NICKEL CATALYST

Expt. no.	$(P_{C_3H_4})^0$ (mm Hg)	$(P_{D_2})^0$ (mm Hg)	$-\Delta P$ (mm Hg)	Fine distribution (%)[a]							$\frac{\phi^b}{100}$
				d_0	d_1	d_2	d_3	d_4	d_5	d_6	
4	30	60	9.0	1.$_9$	18.$_3$	50.$_2$	29.$_0$	0.$_6$	—	—	2.0$_8$
6	30	60	13.2	2.$_4$	18.$_6$	49.$_2$	29.$_2$	0.$_6$	—	—	2.0$_7$
1	30	60	18.0	1.$_8$	18.$_8$	49.$_0$	29.$_7$	0.$_7$	—	—	2.0$_9$
2	30	60	21.$_0$	1.$_8$	18.$_8$	49.$_6$	29.$_1$	0.$_7$	—	—	2.0$_8$
7	30	149	21.$_0$	1.$_8$	17.$_5$	53.$_9$	26.$_7$	0.$_1$	—	—	2.0$_6$

[a] d_i denotes $C_3H_{6-i}D_i$ ($i = 0, 1, 2, \ldots, 6$).

[b] Mean deuterium number, $\phi = \Sigma i \cdot d_i$.

TABLE 2
"HYPERFINE" DISTRIBUTION OF MONO- AND DIDEUTERATED PROPYLENE

Propylene	Isomer: No.				
		trans-1d_1	*cis*-1d_1	2d_1	3d_1
					
Propylene-d_1	2	37.1 ± 3.0	16.7 ± 0.9	45.3 ± 6.7	(0.3 ± 0.1) × 3
	7	38.7 ± 7.4	14.6 ± 1.1	46.7 ± 7.0	<0.2
		cis-1,2d_2	*trans*-1,2d_2	1,1d_2	2,3d_2
					
Propylene-d_2	2	57.7 ± 1.9	25.5 ± 1.9	15.9 ± 2.4	(0.3 ± 0.1) × 3
	7	65.5 ± 1.5	20.4 ± 1.2	13.1 ± 1.2	(0.3 ± 0.1) × 3

given by $C_3H_4 = 98.6\%$ and $C_3H_3D = 1.4\%$. Isotopic composition in the gaseous hydrogen was $H_2{:}HD{:}D_2 = 0.4{:}4.9{:}94.7$ after the reaction (No. 2).

An experiment (No. 5) carried out at the same reaction condition as No. 2 gave a fine distribution (%) of the produced deuteropropane in which highly substituted species are negligibly few.

d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	$\phi/100$
0.$_0$	0.$_3$	2.$_5$	14.$_6$	40.$_0$	39.$_0$	1.$_2$	1.$_2$	1.$_2$	4.$_3$

DISCUSSION

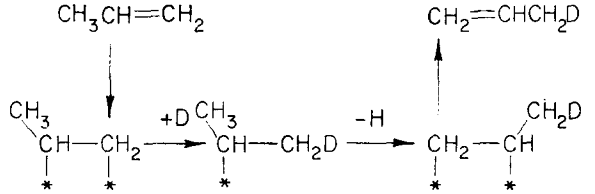
The above results give following interesting findings as well as the result that desorption of methylacetylene is very slow, which can be expected from the reaction of acetylene with deuterium on the $VIII_2$ (Ru, Rh, Pd) and $VIII_3$ (Os, Ir, Pt) group catalysts (*6*).

(A) Highly deuterium-substituted species were not detected in the methylacetylene, propylene, and propane, suggesting that the methyl group is inert to the reaction. This conclusion is decisively evident by the hyperfine distributions of propylene-d_1 and -d_2 in Table 2.

(B) Table 2 indicates that two hydrogen atoms add to the triple bond as the *cis*-form rather than as the *trans*-form. This tendency is shown more evidently by comparing No. 2 with No. 7 when the hydrogen/methylacetylene ratio is large. Besides, as the initial deuterium pressure is increased, the yield of propylene-d_2 and also that of its *cis*-isomer increase relatively, as Table 2 indicates. This corresponds to the tendency observed in the acetylene-deuterium system on Ru, Rh, Pd, and Os, but not on Ir and Pt (*6*, *7*).

(C) Surface protium concentration may be very low as compared with the case of hydrogenation of propylene, because protium is much more adsorbed than deuterium on the surface (*8*), even though the metal catalyst is the same nickel powders.

Finding (A) is quite different from the result obtained in the hydrogenation of propylene on nickel catalyst (*2*); because the hyperfine distribution of propylene-d_1 indicates that methyl position was deuterated in nearly equal amount to methylene position. Therefore, a double-bond migration was proposed to occur during the hydrogenation by Eq. (2) (*9*).



(2)

In the hydrogenation of methylacetylene, however, this process (2) has to be prohibited even as a side step. This conclusion was confirmed by use of the ^{13}C tracer technique in this reaction, because in the hydrogenation of $^{13}CH_3C{\equiv}CH$, the product was only $^{13}CH_3{-}CH{=}CH_2$ but not $CH_3{-}{}^{13}CH{=}CH_2$ nor $CH_3{-}CH{=}{}^{13}CH_2$. The marked difference in the reactivity with deuterium between propylene and methylacetylene may be ascribable to the strong adsorptive power of methylacetylene, so that the adsorbed methylacetylene may play a role of poison to the double-bond migration, though the detailed reason cannot be given yet. This finding is interesting, because in the case of but-2-yne $CH_3C{\equiv}CCH_3$ the double-bond migration occurs on alumina-supported ruthenium or osmium catalyst (*10*), but not on alumina-supported palladium (*11*).

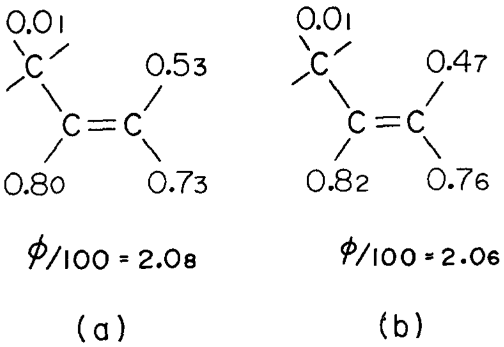


FIG. 2. The mean number of deuterium atoms substituted at each position of hydrogen in propylene which is produced by the reaction of methylacetylene with deuterium on nickel at 25°C: (a) No. 2, $(P_{C_3H_4})^0 = 30$ mm, $(P_{D_2})^0$ 60 mm; (b) No. 7, $(P_{C_3H_4})^0 = 30$ mm, $(P_{D_2})^0 = 149$ mm.

Finding (B) corresponds to the result obtained on acetylene hydrogenation by use of the infrared spectroscopy as a proposition (*12*) and further as a conclusion by Bond *et al.* (*7*); i.e., their reaction was not stereospecific. However, the hydrogenation of but-2-yne was reported to give almost exclusively *cis*-but-2-ene-2,3-d_2 (*11*). Moreover, since only the *cis*-isomer is produced from methylacetylene by the chemical reduction method with zinc and hydrochloric acid (*13*), it may offer an interesting problem from the viewpoint of adsorbed state of methylacetylene. It might be mentioned, however, that fractions of *cis*-isomer to the total d_2-isomers reach about 60% at their yield of about 50%. It will be necessary, therefore, to investigate this point from the stereospecific viewpoint.

Taking the finding (A) into consideration, all the d_3- and d_4-isomers may be composed mainly of $CH_3CD{=}CD_2$ and $CH_2DCD{=}CD_2$, respectively. If it is so, the mean number of deuterium substituted at each position of hydrogen in propylene can be calculated. Two cases, (a) and (b), are shown by Fig. 2, corresponding to different initial ratios of methylacetylene to deuterium, 1/2 and 1/5, respectively.

Figure 2 indicates that the increase of the initial deuterium pressure makes the degree of deuterium substitution increase at the *trans*-1 and 2 positions, but decrease at the *cis*-1 position on the contrary.* This may be due to the relative decrease in the rate of deuterium-exchange as compared with that of hydrogenation; i.e., the latter reaction proceeds more easily than the former.

Finding (C) has to be accounted for by the fact that the very exchangeable hydrogen of methylacetylene is only one methine hydrogen, and also by the slow rate of formation of propane via propyl groups. However, all six hydrogens are exchangeable in the reaction of propylene with deuterium (*2*, *5*). This is the reason why such a marked difference is observable.

The above three findings may be useful not only to elucidate the mechanism of carbon–carbon triple bond hydrogenation, but also to that of poisoning effect of acetylene. Finally an important finding not pointed out above is added; i.e., methylacetylene-d_1, $CH_3C{\equiv}CD$, seems to exist on the surface in comparatively large concentration, judging from much production of propylene-1,1-d_2, propylene-*trans*-1,2-d_2 and propylene-*cis*-1-d_1 isomers. Detailed discussion on the total reaction mechanism including the above possibility will be published elsewhere.

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* *Cis*-1 and *trans*-1 denote the methylene hydrogen with reference to the methyl group, while 2 denotes the methine hydrogen.