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Catalytic Hydrogenation
of
Methylacetylene over Group VIII Metals

—— Application of Microwave Spectroscopy to the
Analysis of Isomeric Deuteropropylenes ——

By
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Thesis submitted to Osaka University
for the degree of Doctor of Science

1971

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Chapter I. INTRODUCTION

The catalytic hydrogenation of acetylenic compounds presents many problems which are essentially different from those encountered in mono-olefine hydrogenation. Main points in the problems lie in how the reaction may be stopped at the olefine stage, and whether the olefine has a cis or trans configuration. They are of great importance not only in organic synthesis but also for elucidation of the mechanism of the heterogeneous catalysis. In the industrial investigations considerable efforts were devoted especially to obtain high yields of olefines from acetylenes by hydrogenation. In the fundamental aspects, however, since the hydrogenation of acetylene over nickel was found by Sabatier et al. in 1899,¹⁾ a few studies were made on this reaction. The mechanism of catalytic hydrogenation of acetylenic compounds was not discussed in details until now, except that the mechanism for acetylene hydrogenation was proposed on the basis of kinetic informations by Bond et al.²⁾

In order to study the mechanism of catalytic hydrogenation reactions, deuterium is known to be a powerful isotope as a tracer. With the aid of modern analytical instruments it is possible to learn about the details of deuterium distributions. Mass-spectrometric

analysis, used extensively for determining the deuterium distribution till now, gives us the knowledge about the deuterium content, while nmr and infrared spectroscopic analysis give us finer informations on the substituted position of deuterium atoms. Therefore, to apply deuterium as an isotopic tracer to this system may give light on the mechanism of the reaction.

However, little work were published until now on the hydrogenation of acetylenic compounds with deuterium over metal catalysts. Such a situation is surprising in view of an enormous number of research for olefine hydrogenation where deuterium was utilized as a tracer.³⁾

In 1939, Farkas and Farkas⁴⁾ studied the hydrogenation of acetylene with deuterium over platinum foil, using the thermal conductivity technique, and they reported that formed deuteroacetylene and HD were found negligible, judging by the return of light hydrogen to the gas phase.

In 1950, Arnett and Crawford⁵⁾ attempted to prepare cis-ethylene-d₂ alone by the palladium-catalyzed hydrogenation of acetylene with deuterium, but they obtained all possible deuteroethylenes, which were examined by the mass and infrared spectrometry.

In 1953, Douglas and Ravinovitch,⁶⁾ were also unable

to produce cis-ethylene-d₂, using nickel-kieselguhr at room temperature, but they found that lowering the temperature to -80° increased the yield of trans-ethylene-d₂. Furthermore, they pointed out that simultaneous addition of hydrogen to the triple bond appeared to be ruled out from the experimental data, using equilibrated and non-equilibrated mixtures of hydrogen and deuterium.

More recently, Bond et al.^{7),8)} used the mass and infrared spectrometric methods to study the reaction between acetylene and deuterium over noble Group VIII metals supported on alumina. They determined quantitatively the distribution of isomeric didutero-ethylenes, such as cis-, trans- and asymmetric-ethylene-d₂. Even though the distribution varied from metal to metal, the yield of cis-isomer was related to the fraction of total ethylene-d₂. Moreover, they interpreted the distribution by applying the steady state treatment, proposed by Kemball⁹⁾ for hydrogenation and exchange of ethylene over metal films.

For the higher acetylenic compounds, reduction of dimethylacetylene by deuterium was studied by Meyer and Burwell¹⁰⁾ over palladium-alumina, and also by Webb, Wells and Philipson¹¹⁾ over the other noble Group VIII metals. The former group of workers used the mass and

nmr spectrometric methods and pointed out that deuterium atoms in the formed cis-2-butene almost localized at carbon atoms 2 and 3. They extended this method to the hydrogenation of ethylacetylene, 1,2-butadiene and 1,3-butadiene,¹²⁾ and investigated the mean number of deuterium atoms which were substituted in all positions of the produced butenes.

Thus the reaction of deuterium with acetylene, dimethylacetylene or ethylacetylene were studied already, though small in number. For the catalytic hydrogenation of methylacetylene, only the kinetic studies were reported,^{13), 14)} but no tracer study using deuterium was published.

In order to investigate the mechanism of hydrogen addition to the carbon-carbon triple bond, methylacetylene is a more suitable compound than acetylene, because of the following reasons. i) Methylacetylene has three carbon atoms of different character, while acetylene has two equivalent carbons. Therefore, differences of catalytic behavior for deuteration of methylacetylene will be revealed more obviously than that of acetylene. ii) Methylacetylene may offer more detailed information on the stereospecific hydrogenation than acetylene, because the isotopic isomers of propylene- d_1 and $-d_2$ (see Fig. 3) can be produced by the reaction

of methylacetylene with deuterium. iii) Methylacetylene is a higher acetylenic compound next to acetylene. The distribution of isotopic isomers of deuteropropylene, therefore, gives us the information which can be extended to the hydrogenation of higher acetylenic compounds; for example, the information related to isomerization of olefine accompanying the double bond migration which often proceeds during the hydrogenation.¹⁵⁾

The first purpose of this thesis is to clarify the mechanism of catalytic hydrogenation of methylacetylene, and the second purpose to examine the characteristic behavior of Group VIII metals for this reaction. For these purposes the reaction of methylacetylene with deuterium is mainly investigated over Ni, Pd, Pt, Rh, Ir and Ru catalysts at the same condition. The distributions of deuteromethylacetylene and deuteropropylene produced by the reaction are determined by mass spectrometry, while the distributions of isotopic isomers of propylene-d₁ and -d₂ by microwave spectrometry. Though the latter new technique was not applied hitherto, much information will be given by it on the stereochemical problems in the mechanism as well as on the chemisorbed state of the reactants.^{15),16),25)} The third purpose is ascertain how the isomerization of methylacetylene to allene ($\text{CH}_3\text{-C}\equiv\text{CH} \longrightarrow \text{CH}_2=\text{C}=\text{CH}_2$) is related to the

hydrogenation of methylacetylene over six metals, because allene is found to appear during the hydrogenation of methylacetylene at 25° over ruthenium-black. Experimentally, the isomerization reactions between methylacetylene and allene are carried out over these metals especially in details over ruthenium-black.

Chapter II. EXPERIMENTAL

1. Materials

Methylacetylene (Takachiho Chem. Ind. Co.), containing about 5 % impurities such as propylene, acetylene and allene, was purified by freezing out of carrier gas stream on elution from a gas chromatograph, in which a column of dimethylsulforane on neopak-1B was charged and was operated at the room temperature. In succession the methylacetylene thus purified was distilled under vacuum using liquid nitrogen and solid carbon dioxide as refrigerants. By gas chromatography the final purity was determined to be better than 99.7 %.

Allene (Takachiho Chem. Ind. Co.), containing about 95 % allene, was purified in the same procedure as methylacetylene. The purity was also increased to 99.7 % or better.

Deuterium (Takachiho Chem. Ind. Co.) was sufficiently pure for the present purpose, because impurities were not detected by gas chromatography. The isotopic purity was found better than 99.5 % by mass spectroscopic analysis.

Electrolytic hydrogen was purified by passing it over silicagel, hot copper wire at 350° and through a liquid nitrogen trap, successively.

2. Catalysts

Nickel powders were prepared by thermal decomposition of nickel formate, which had been dried in vacuum at 170° for 1 hr, raising the temperature gradually up to 350° . Then nickel powders were degassed at 350° for 2 hrs and were reduced with hydrogen at 250° overnight before the experiments. Nickel formate was precipitated by formic acid from a nickel carbonate solution.

Rhodium-black was prepared by the reduction of rhodium hydroxide, produced by the reaction of a rhodium trichloride solution with a sodium hydroxide solution. The rhodium metal thus obtained was washed with distilled water and was dried in vacuum.

Iridium-black was prepared by adding a 0.01 mol solution of iridium tetrachloride to excess amount of a hot solution of sodium borotetrahydride. Iridium-black thus precipitated was washed repeatedly with hot distilled water and dried at 100° .

Palladium-black, platinum-black (Nakarai Chem. Ltd.) and ruthenium-black (Mitsuwa Pure Chem. Co.) of commercial reagents were used.

All the catalysts above mentioned were reduced with hydrogen at 230° - 240° for two days in the reaction vessel before the experiments.

3. Hydrogenation

The hydrogenation of methylacetylene with deuterium was carried out under the same condition on all the six metal catalysts. Main parts of the apparatus used for hydrogenation are shown in Fig. 1. They are connected to a conventional vacuum system and to gas reservoirs.

Before each run the catalysts were treated with hydrogen at $230^{\circ}\sim 240^{\circ}$ overnight, in order to remove the deuterium which remained on the catalysts. Then the catalysts were degassed for 3 hr at the same temperature, and were cooled down to the reaction temperature ($25^{\circ}\pm 0.2^{\circ}$) if not described otherwise. The reaction vessel was immersed in a water thermostat.

"The standard mixture" which consisted of $P_{D_2} = 60$ mm and $P_{C_3H_4} = 30$ mm was introduced into the reaction vessel. Reactions were carried out in a simple static system and followed from manometric measurement. When a desired degree of hydrogenation was reached, the reaction mixture was taken out by expanding it into a reservoir (3 l) preliminarily evacuated. The products were analyzed by gas chromatography, mass and microwave spectroscopy.

In order to avoid the reaction to be diffusion-controlled, the amount of catalyst was adjusted to obtain a condition under which the half-life of the

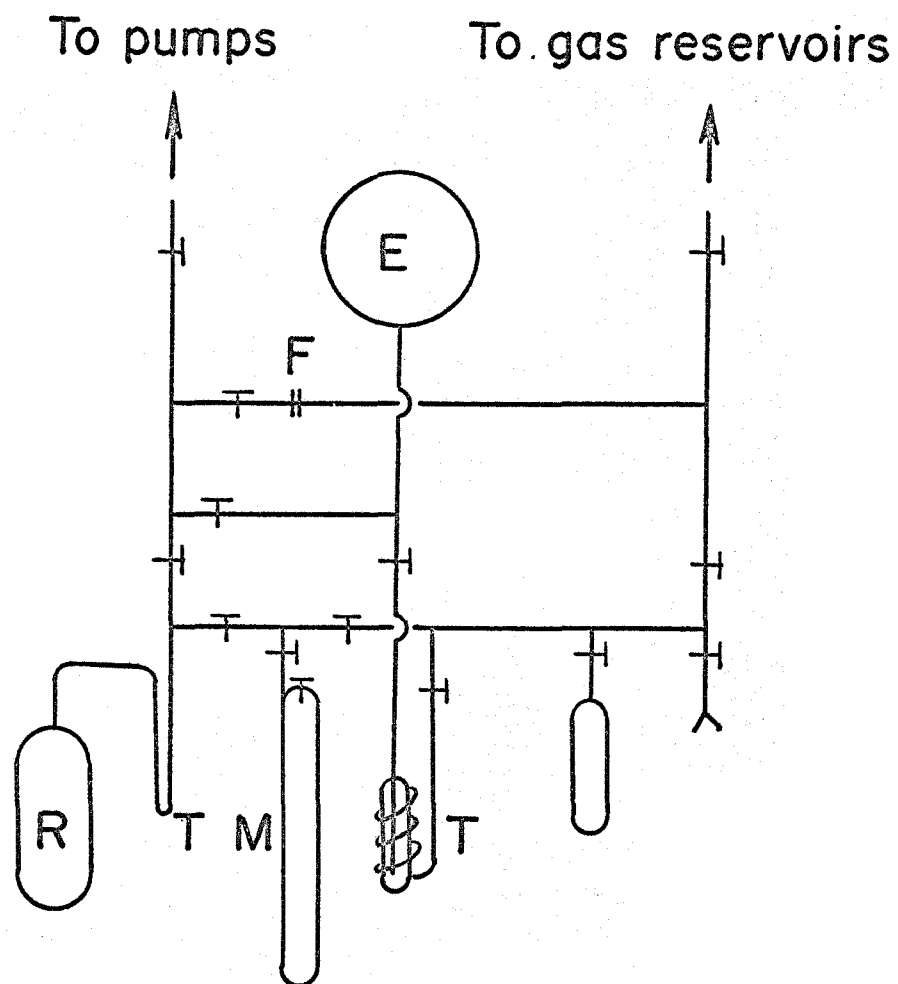


Fig. 1. Apparatus for the study of hydrogenation
 R, reaction vessel; T, trap; M, manometer;
 F, glass filter; E, Expansion reservoir.

reaction (15 mm of the total pressure fall) lay in the ranges 1-2 hr. Volume of the reaction vessels and amount of the catalysts used for the hydrogenation are listed in Table 1, together with their BET surface area. The BET surface area of each metal catalyst was measured by using nitrogen as the adsorbent at -198° .

4. Isomerization

The isomerization between methylacetylene and allene over ruthenium-black catalyst (0.12 g) was also investigated in a static system. The apparatus used in the study is shown in Fig. 2. In order to analyze the composition of the reaction products continually, a sampling tube (2-3 ml) with two stopcocks was directly connected to a reaction vessel (about 600 ml) at an end, and the other end of the tube was placed in the steady flow of carrier gas (He), which led each sample to a gas chromatograph.

After hydrogen treatment and degassing of the catalyst in the same manner as used in the study of hydrogenation, known amount of methylacetylene or allene was introduced into the reaction vessel. At arbitrary intervals of time, a small amount of the reaction mixture was taken out into the sampling tube preliminarily evacuated and was analyzed by gas chromatography.

Table 1

The volume of reaction vessels and the amount of catalysts used for the hydrogenation of methylacetylene.

Catalysts	BET Surface Area *) (m ² /g)	Amount of Cat. (mg)	Volume of reaction vessels (ml)
Ni	2.1	100	330
Pd	7.7	2	330
Pt	2.4	40	260
Rh	10.9	30	310
Ir	14.2	20	270
Ru	33.2	150	370

*) The surface area of each metal catalyst was measured by using nitrogen at -198°.

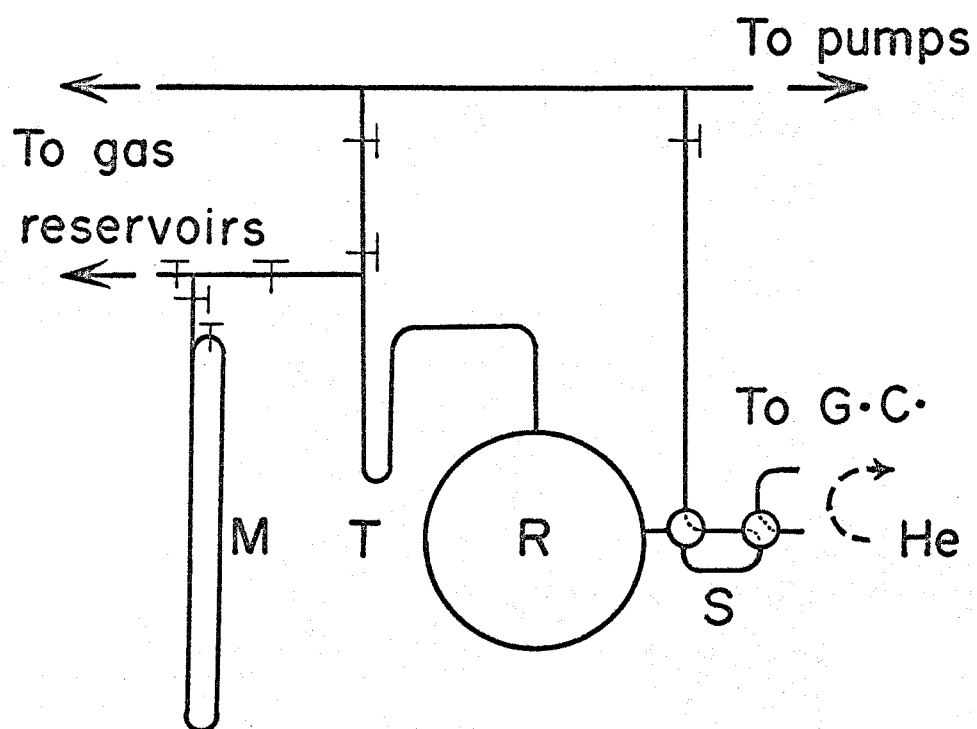


Fig. 2. Apparatus for the study of isomerization
 R, reaction vessel; S, sampling tube for gas
 chromatographic analysis; M, manometer;
 T, trap.

Loss of the reaction mixture by sampling was about 0.4 % of its total amount in the vessel, and an analytical result obtained by this method coincided within an experimental error with a value of the sample, which was obtained by condensing all of the same reaction mixture by liquid nitrogen.

5. Analysis

Composition of hydrocarbons produced by the hydrogenation and isomerization was analyzed by gas chromatography using helium as the carrier gas with a 4-m column of 20 wt % dimethylsulforane on neopak 1B (D.M.S.) at 25°. Area under each component peak in a gas chromatogram was determined by the product of the half-peak width and peak height. Sensitivity factors adopted were as follows.

$$\text{C}_3\text{H}_8 = 1.00, \quad \text{C}_3\text{H}_6 = 0.96, \quad \text{C}_3\text{H}_4 = 0.92$$

These values were obtained from the average of four measurements using an equimolal mixture of propane, propylene, allene and methylacetylene.

Samples for mass and microwave spectrometric analysis in the study of the hydrogenation was prepared with a gas chromatograph. First, methylacetylene was separated from propane and propylene by using a DMS

column, and second, propylene from propane by using a silicagel column at 80°. Eluted fractions were condensed separately into receivers cooled in liquid nitrogen. Retention times were as follows.

	Propane	Propylene	Methylacetylene
D.M.S. (25°)	5 min	7 min	25 min
Silicagel(80°)	7.5 min	17 min	

Distributions of deuteropropylene and deuteromethylacetylene were analyzed with a mass spectrometer (Hitachi RMU-5B), installed at the Institute for Protein Research, Osaka University. In this analysis the energy of the ionizing electrons was lowered sufficiently so that only the parent ion was produced.

The microwave spectrometric method was applied in order to determine the relative abundance of isotopic isomers of monodeuteropropylene (C_3H_5D) and dideuteropropylene ($C_3H_4D_2$), measuring the intensities of rotational $1_{01} \leftarrow 0_{00}$ transition of their various species. The spectrometer used was the conventional Hughes-Wilson type or the Stark modulation spectrometer, and was installed at the Sagami Chemical Research Center. All measurements were done at dry ice temperature.

Terminology

"Selectivity (S)" is used hereafter to denote the yield of propylene produced by the hydrogenation of methylacetylene, and this term is defined as follows.

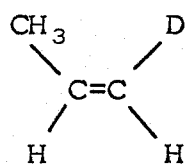
$$S = P_{C_3H_6} / (P_{C_3H_8} + P_{C_3H_6})$$

Propylene-d₁ (C₃H₅D) and -d₂ (C₃H₄D₂) have four and seven species of their isotopic isomers, respectively, as shown in Fig. 3. The distribution of these isomers will be called "hyperfine distribution (h.f.d.)" in order to discriminate it from the usual deuterium distribution or "fine distribution (f.d.)", which is determined by mass spectroscopy and which gives only knowledge on the number of deuterium atoms substituted in some compounds, such as propylene-d₁, -d₂ and so on.

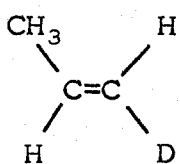
"Conversion" of hydrogenation is defined by the percentage of the total pressure decrease to the initial pressure of methylacetylene. In the reaction with the standard mixture ($P_{C_3H_4} = 30$ mm and $P_{D_2} = 60$ mm), therefore, the total pressure fall of 60 mm which is expected in the complete reaction $C_3H_4 + 2H_2 = C_3H_8$ corresponds to 200 % conversion.

Fig. 3. Isotopic isomers of propylene- d_1 and $-d_2$, and their names

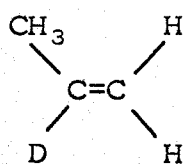
Propylene- d_1



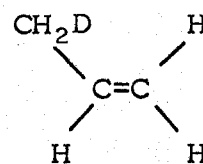
cis-1- d_1



trans-1- d_1

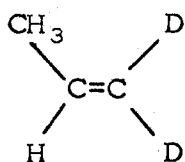


2- d_1

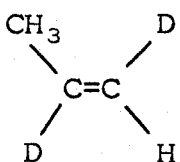


3- d_1

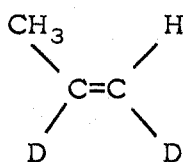
Propylene- d_2



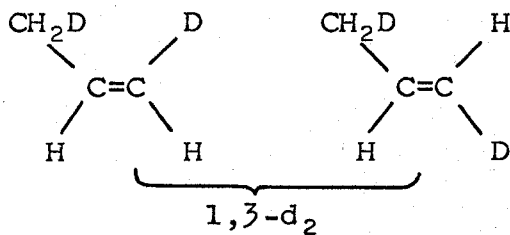
1,1- d_2



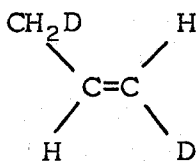
trans-1,2- d_2



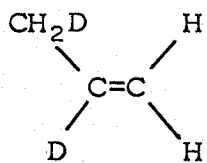
cis-1,2- d_2



1,3- d_2



2,3- d_2



3,3- d_2

Chapter III. RESULTS

Part A. Hydrogenation

From the recent studies of the hydrogenation of methylacetylene^{13),14)} over supported or unsupported Group VIII metals, following conclusions are derived. The initial rate order in hydrogen lies in the ranges 1.0~1.3, while the order in methylacetylene is zero or slightly negative. Polymerization appears to be detected in a somewhat greater extent during the hydrogenation over all the catalysts.

In the present investigation, the reaction of methylacetylene with deuterium was carried out, therefore, at a relatively low temperature (25°) so that the possible occurrence of polymerization might be minimized. Actually, no polymerization was observed, and all metal catalysts, except nickel, retained steady activities for sufficient periods to give consistent results. Nickel was deactivated, however, and its activity decreased to 2/3 of the initial one after five experiments.

A-1. Reaction curves

Typical reaction curves with a mixture of hydrogen and methylacetylene (H_2 or D_2 : $CH_3-C\equiv CH$ = 2 : 1) over six metal catalysts are shown against time in Fig. 4. All

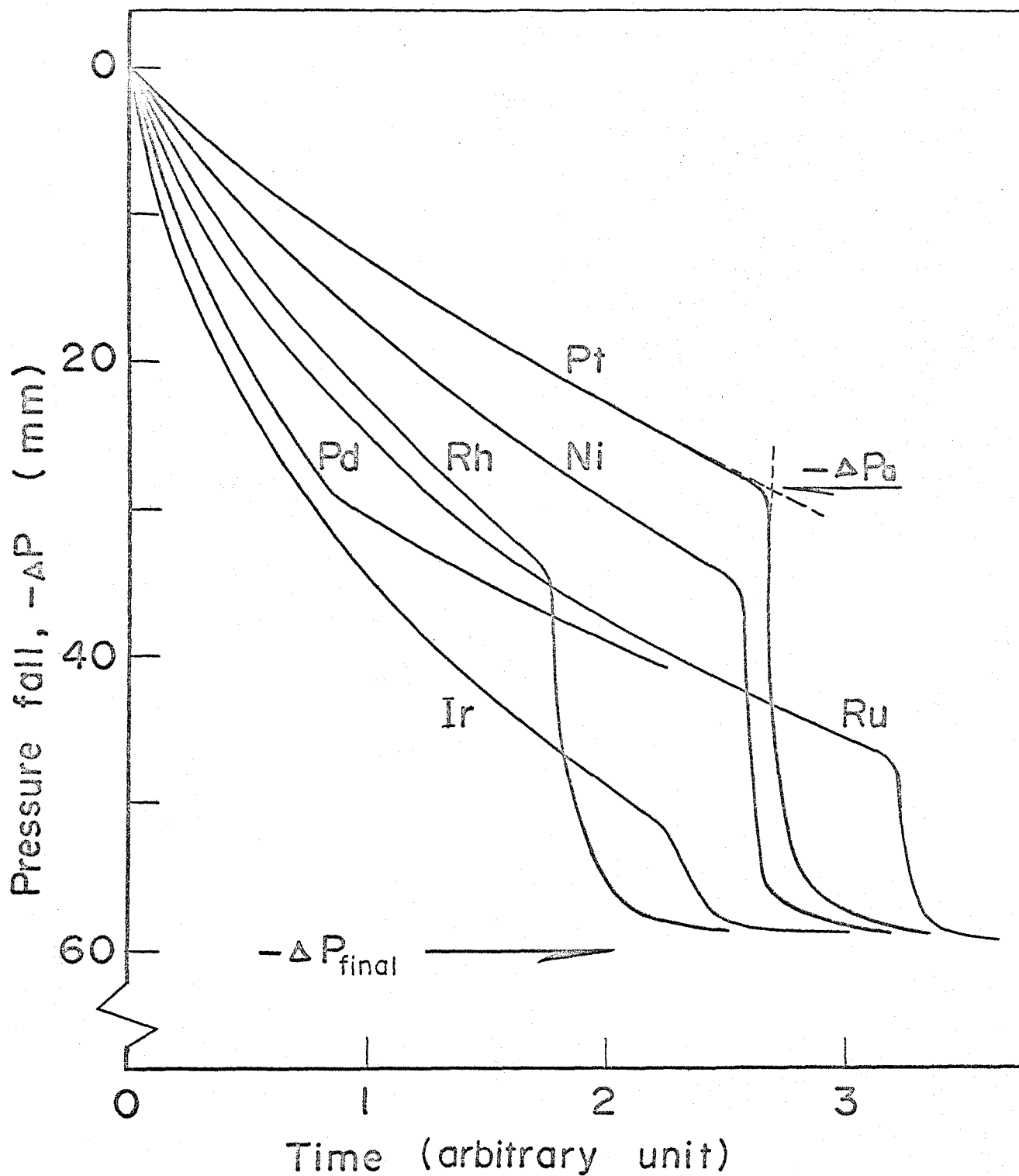


Fig. 4. Typical pressure fall ($-\Delta P$) against time curves for the hydrogenation of methylacetylene at 25° .

Ni, Pt, Ir, $(P_{\text{H}_2})^\circ = 60$ mm and $(P_{\text{C}_3\text{H}_4})^\circ = 30$ mm;
 Pd, Rh, Ru $(P_{\text{D}_2})^\circ = 60$ mm and $(P_{\text{C}_3\text{H}_4})^\circ = 30$ mm.

the curves ($-\Delta P$ vs. time) seem practically to consist of two parts of different rates. Each part is regarded to correspond to a stage. The rapid acceleration in the second stage was observed over all metals except palladium, where the rate of the second stage was slower than that of the first.

The acceleration points ($-\Delta P_a$) defined by the pressure obtained by the intersection of the curved portions of the first and second stage of the reaction (Fig. 4) appeared at the pressure fall of about 34.3 mm over Ni, 34 mm over Rh, 29.1 mm over Pd and Pt, 51.4 mm over Ir, and 46.5 mm over Ru. Over all the six metal catalysts, the total pressure fall observed near the end of the reaction was very close to that expected from the stoichiometric equation $C_3H_4 + 2H_2 = C_3H_8$, so that any polymerization process may be neglected in the present reaction conditions. Actually, volatile polymers were not detected in the reaction mixture of the hydrogenation by a gas chromatograph.

The rates of pressure fall during the course of the first stage reaction was approximately proportional to the first power of the remaining hydrogen pressure, as shown by the first-order rate plots for the reaction over Ni, Pd and Rh in Fig. 5. This finding is in accord with the kinetic data reported by Bond et al.¹³⁾

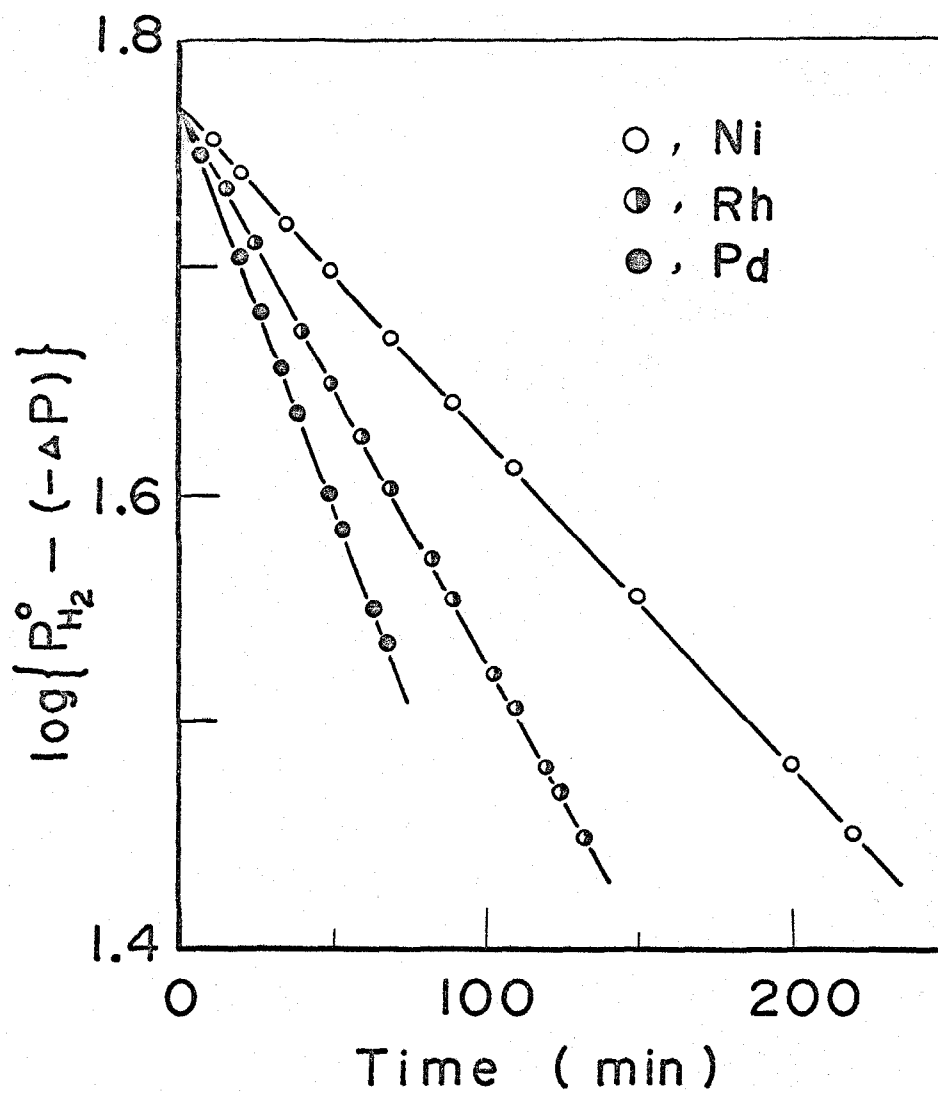


Fig. 5. First order rate plots of the hydrogenation of methylacetylene over Ni, Pd-black and Rh-black at 25°.

Pd, Rh, $(P_{C_3H_4})^0 = 30$ mm and $(P_{D_2})^0 = 60$ mm;

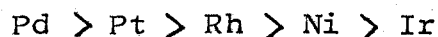
Ni, $(P_{C_3H_4})^0 = 30$ mm and $(P_{H_2})^0 = 60$ mm.

and Mann et al.¹⁴⁾ recently for the hydrogenation of methylacetylene using pumice-supported and unsupported metal catalysts of Group VIII; i.e., practically first order in hydrogen and zero or slightly negative order in methylacetylene.

The effect of initially added propylene upon the hydrogenation rate was studied over iridium-black catalysts. The reaction curve observed with the mixture which consisted of 30 mm of methylacetylene, 26 mm of propylene and 60 mm of duterium agreed well with that observed with the standard mixture. Thus no effect of added propylene was observed.

A-2 Selectivity

The course of the reaction with the standard mixture was followed by analyzing the reaction products after various conversions, and the selectivity (S) was determined. Fig. 6 shows the dependence of selectivity on conversion of the hydrogenation. The selectivity was constant within an experimental error, during the course of the first stage for all the catalysts and the sequence in S at 25° was as follows.



The typical values of selectivity over six metal catalysts

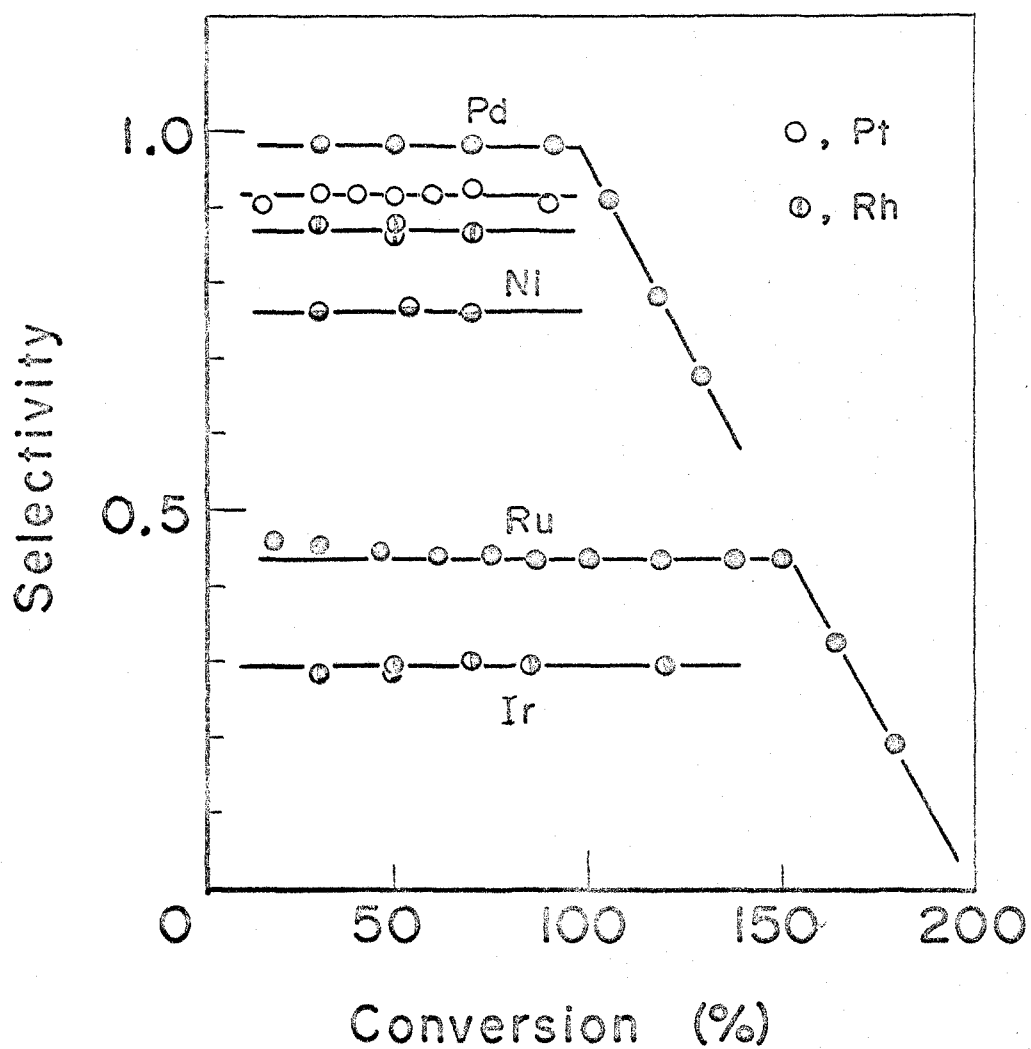


Fig. 6. Selectivity against conversion curves for the hydrogenation of methylacetylene at 25°.

$$(P_{D_2})^0 = 60 \text{ mm}, \quad (P_{C_3H_4})^0 = 30 \text{ mm}.$$

are summarized in Table 2.

For the reaction over Pd and Ru, the selectivity was determined not only in the first stage, but also in the second stage, as shown in Fig. 6. Selectivity vs. conversion curves of both metals were consisted of two straight lines, which intersected at the conversion corresponding to the acceleration point. After the point, the selectivity decreased rapidly as the reaction proceeded. This finding shows clearly that in the first stage methylacetylene is hydrogenated to both propylene and propane in a certain ratio, and that in the second stage further hydrogenation of propylene to propane becomes dominant.

During the hydrogenation catalyzed by ruthenium-black, a trace amount of allene, an isomer of methylacetylene, was produced in addition to the hydrogenation products. Over the other metal catalysts (Ni, Pd, Pt, Rh and Ir), however, allene could not be detected in the reaction products.^{*)} Table 3 shows the composition of hydrocarbons at three conversions of the hydrogenation over ruthenium-black. As is seen from Table 3, the amount of allene increased as the reaction proceeded.

^{*)} This point is clarified in p. 65.

Table 2

Selectivity (S) for Propylene Formation during
the Reaction of Methylacetylene (30 mm) and
Deuterium (60 mm) at 25°.

Conv. (%)	Ni	Pd	Pt	Rh	Ir	Ru
30	0.76	0.98	0.92	0.88	0.28	0.45
50	—	0.98	0.91	0.88	0.28	0.45
70	0.76	0.98	0.92	0.86	0.30	0.43

Table 3

Percentage Composition of Hydrocarbons in the
Reaction Mixture of $C_3H_4 + D_2$ over Ru-black at 25°.

No.	Conv. (%)	Propane	Propene	Allene	MA
57	30	11.5	9.6	1.4	77.5
55	50	17.8	14.3	1.2	66.3
56	70	24.2	18.4	4.3	53.1

A-3 Fine and hyperfine deuterium distributions

The deuteropropylene formed by the reaction of methylacetylene with deuterium as well as the residual methylacetylene were analyzed mass spectrometrically, and the fine deuterium distributions were determined. Mono- and di-deuteropropylenes were also examined by microwave spectroscopy to determine their hyperfine deuterium distributions. All the runs were analyzed in the first stage, namely before the acceleration point.

The results are shown in Tables 4 (Ni), 5 (Pd), 6 (Pt), 7 (Rh), 8 (Ir), and 9 (Ru). Each table is divided into two sections, such as Table 4f for the fine distributions and Table 4h for the hyperfine distributions. In the "f" sections of the tables, $\bar{\Phi}/100$ denotes the mean number of substituted deuterium atoms in the produced propylene. They are calculated by $\bar{\Phi}/100 = \sum i \cdot d_i / 100$, where $i = 0, 1, \dots, 6$, and d_i is the percentage composition of propylene- d_i ($C_3H_{6-i}D_i$). The measurement errors in the hyperfine deuterium distributions are indicated by the values of 2.5σ (σ : the standard deviation).

1) Nickel catalyst. Table 4f indicates that propylene- d_2 is the major product during the reaction over nickel catalyst, and that the fine distribution of deuteropropylene is constant until 70 % conversion.

Nevertheless, the degree of deuterium exchange in methylacetylene was very small. Isotopic composition of the residual deuterium was also examined by mass spectrometry for the experiments No.2 and No. 3.

The results were $H_2 : HD : D_2 = 0.2 : 2.2 : 97.6$ (No. 3) at the 30 % conversion, and $0.4 : 4.9 : 94.7$ (No. 2) at the 70 % conversion. Thus the return of hydrogen to the gas phase was very small, though increased to some extent as the reaction proceeded.

When the initial deuterium pressure was increased from 60 mm to 149 mm, the yield of propylene- d_2 increased and the mean number of substituted deuterium atoms in propylene ($\bar{\Phi}/100$) decreased slightly. An increase in temperature from 0° to 50° reduced the yield of propylene- d_2 and favored highly deuterium-substituted species, such as propylene- d_3 , $-d_4$, $-d_5$, and $-d_6$.

The hyperfine distributions of propylene- d_2 are summarized in Table 4h, where the percentage composition of only four isomers are described, because other three possible isomers of propylene- d_2 could not be detected. Of the propylene- d_2 isomers, cis-1,2- d_2 is the most abundant product in all the cases. Increase of the initial partial pressure of deuterium increased the yield of cis-1,2- d_2 , but decreased those of trans-1,2- d_2 and 1,1- d_2 . The yield of Propylene-cis-1,2- d_2

was reduced by increasing the temperature.

The amounts of propylene-3-d₁ and propylene-2,3-d₂ were very small. Moreover, microwave analysis of propylene-d₃ (No. 2) gave the results that the greater part of propylene-d₃ is propylene-1,1,2-d₃, CH₃-CD=CD₂. Thus, the methyl group of the methylacetylene is inert to the reaction over the nickel catalyst. This conclusion was confirmed in the hydrogenation of ¹³CH₃-C≡CH, because the produced propylene was only ¹³CH₃-CH=CH₂ but not CH₃-¹³CH=CH₂ nor CH₃-CH=¹³CH₂. These results are summarized in Table 10.

Table 4f

Nickel-Catalyzed Reaction

Fine Distributions of Deuteropropylene and Deuteromethylacetylene.

No.	$P_{MA}^O/P_{D_2}^O$ ^{a)}	Conv. (%)	Temp. (°C)	Methylacetylene(%)			Propylene (%)								Φ 100
				d ₀	d ₁	≥ d ₂	d ₀	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆		
3	1/2	30	25	99.5	0.5	—	1.9	18.3	49.8	29.5	0.6	—	—	2.0 ₉	
4	1/2	30	25	99.4	0.6	—	1.9	18.3	50.2	29.0	0.6	—	—	2.0 ₈	
6	1/2	44	25				2.4	18.6	49.2	29.2	0.6	—	—	2.0 ₇	
1	1/2	60	25	99.3	0.7	—	1.8	18.8	49.0	29.7	0.7	—	—	2.0 ₉	
2	1/2	70	25	98.6	1.4	—	1.8	18.8	49.6	29.1	0.7	—	—	2.0 ₈	
5	1/2	70	25	98.4	1.6	—	2.0	18.4	49.6	29.7	0.3	—	—	2.0 ₈	
7	1/5	70	25	98.8	1.2	—	1.8	17.5	53.9	26.7	0.1	—	—	2.0 ₆	
13	1/2	70	0	99.6	0.4	—	1.8	18.6	52.6	26.7	0.3	—	—	2.0 ₅	
14	1/2	70	50	98.2	1.8	—	2.3	16.4	46.8	32.6	0.9	0.5	0.5	2.1 ₇	

a) $P_{MA}^O = 30$ mm

Table 4h (Nickel)
Hyperfine Distribution of Propylene-d₁ and -d₂

No.	Conditions	Conv. (%)	Propylene-d ₁				Propylene-d ₂			
			c-1-d ₁	t-1-d ₁	2-d ₁	3-d ₁	c-1,2-d ₂	t-1,2-d ₂	1,1-d ₂	2,3-d ₂
4	1/2, 25°	30	15.2 ± 1.0	39.9 ± 6.9	45.5 ± 5.1	< 1.2	59.5 ± 1.6	24.9 ± 2.0	15.6 ± 1.8	< 0.5
2	1/2, 25°	70	16.7 ± 0.9	37.1 ± 3.0	45.3 ± 6.7	0.9 ± 0.3	57.7 ± 1.9	25.5 ± 1.9	15.9 ± 2.4	0.9 ± 0.2
7	1/5, 25°	70	14.6 ± 1.1	38.7 ± 7.4	46.7 ± 4.0	< 0.2	65.5 ± 1.5	20.4 ± 1.2	13.1 ± 1.2	1.0 ± 0.3
13	1/2, 0°	70	19.3 ± 1.1	33.5 ± 4.5	46.6 ± 4.7	0.6 ± 0.2	57.2 ± 0.9	28.5 ± 0.9	14.3 ± 1.5	< 0.2
14	1/2, 50°	70	19.7 ± 0.9	32.9 ± 4.5	46.6 ± 3.0	0.8 ± 0.3	48.9 ± 1.0	29.8 ± 2.6	21.3 ± 0.6	< 0.2

2) Palladium catalyst. For the reaction of methylacetylene with deuterium over palladium-black catalyst, the fine and hyperfine distributions of deuteropropylene were examined not only in the first stage but also in the second stage (after 97 % conversion). They are listed in Table 5f and 5h, respectively.

In the first stage of the reaction, the yield of propylene-d₂ and that of propylene-cis-1,2-d₂ were larger than those obtained from the nickel-catalyzed reaction. Highly deuterium-substituted propylenes (propylene-d₄, -d₅ and -d₆) were not detected. This finding indicates that the methyl group was not substituted by deuterium. This conclusion is decisively evident by the hyperfine distributions of propylene-d₁ and -d₂ in Table 5h.

The degree of deuterium exchange in methylacetylene as well as the return of hydrogen to the gas phase were very small even at 50 % conversion (No. 16), judging from the following results.

$$\text{C}_3\text{H}_4 = 98.1 \%, \quad \text{C}_3\text{H}_3\text{D} = 1.9 \%$$

$$\text{H}_2 = 0.2 \%, \quad \text{HD} = 1.9 \%, \quad \text{D}_2 = 97.9 \%$$

During the first stage of the reaction, both deuterium distributions were constant and the methyl group was not substituted by deuterium. In the second stage, however, highly deuterium-substituted propylenes

were produced and the methyl group was substituted by deuterium as shown in Table 5h (No. 42). Moreover, the yield of those species increased as the reaction proceeded.

This tendency is due to the occurrence of propylene isomerization in the second stage, which is prohibited in the first stage. This result agrees well with the hydrogenation of dimethylacetylene catalyzed by alumina-supported palladium;¹⁷⁾ i.e., the reaction was highly selective for the formation of cis-2-butene in the first stage, but after the removal of dimethylacetylene the cis-2-butene isomerized to trans-2-butene and 1-butene as well as hydrogenated.

Table 5f
Palladium-Catalyzed Reaction (25°)
Fine Distribution of Deuteropropylene

No.	Conv. (%)	Propylene (%)							$\frac{\Phi}{100}$
		d ₀	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆	
16	50	1.1	11.1	79.2	8.6	—	—	—	1.9 ₅
15	70	0.9	11.6	78.5	9.0	—	—	—	1.9 ₆
44	90	0.8	9.1	79.2	10.9	—	—	—	2.0 ₀
43	105	0.7	9.1	72.9	15.3	0.9	0.6	0.5	2.1 ₀
42	118	0.8	9.0	63.9	21.7	2.2	1.4	1.1	2.2 ₄
41	130	0.9	8.3	50.1	29.2	5.4	3.6	2.6	2.5 ₁

$P_{C_3H_4}^O = 30 \text{ mm}, \quad P_{D_2}^O = 60 \text{ mm}$

Table 5h (Pd)

Hyperfine Distribution (%) of C_3H_5D and $C_3H_4D_2$

No.	Conv. (%)	Propylene- d_1			propylene- d_2			
		c-1- d_1	t-1- d_1	2- d_1	1,1- d_2	t-1,2- d_2	c-1,2- d_2	2,3- d_2
17	30	5.7 ± 0.4	51.6 ± 8.2	42.7 ± 4.9	0.7 ± 0.3	10.4 ± 0.5	88.9 ± 0.6	---
16	50	5.5 ± 0.3	49.7 ± 6.2	44.8 ± 4.7	0.9 ± 0.1	10.6 ± 0.7	88.5 ± 0.6	---
15	70	5.7 ± 0.5	49.8 ± 7.8	44.6 ± 8.2	1.0 ± 0.1	11.3 ± 0.5	87.7 ± 0.5	---
42	118	8.3 ± 0.5	38.9 ± 3.4	52.8 ± 7.1	2.3 ± 0.1	16.3 ± 0.5	79.9 ± 0.5	1.4 ± 0.2

$$P_{C_3H_4}^O = 30 \text{ mm}, \quad P_{D_2}^O = 60 \text{ mm}, \quad 25^\circ$$

3) Platinum catalyst. Features of both deuterium distributions obtained over Pt-black catalyst showed a general similarity to those obtained over Pd-black catalyst, except that propylene-d₄ was produced over Pt-black, as Table 6 shows, though small in amount.

The major products were propylene-d₂ in propylene, and propylene-cis-1,2-d₂ in propylene-d₂. Both distributions were constant within an experimental error during the first stage of the reaction. The isomers, in which the methyl group was substituted by deuterium, were not detected in both propylene-d₁ and -d₂.

The exchange degree of methylacetylene with deuterium was very small, though it increased gradually as the reaction proceeded. Isotopic composition of deuterium at 70 % conversion (No.23) was as follows.

$$H_2 = 0.3 \%, \quad HD = 2.1 \%, \quad D_2 = 97.6 \%$$

Thus the return of hydrogen to the gas phase was very small in the same manner as observed over nickel and palladium-black catalysts.

Table 6f

Platinum-Catalyzed Reaction (25°)

Fine Distribution (%) of Deuteromethylacetylene and Deuteropropylene

No.	Conv. (%)	Methylacetylene			Propylene						Φ
		d ₀	d ₁	≥ d ₂	d ₀	d ₁	d ₂	d ₃	d ₄	d ₅ , d ₆	100
25	30	97.2	2.8	—	1.3	14.5	74.7	9.2	0.3	—	1.9 ₃
26	40	97.0	3.0	—	1.3	14.1	75.0	9.4	0.2	—	1.9 ₃
24	50	96.9	3.1	—	1.1	14.0	75.0	9.3	0.6	—	1.9 ₄
23	70	96.8	3.2	—	1.0	13.4	75.2	9.8	0.5	—	1.9 ₅

$P_{C_3H_4}^O = 30 \text{ mm},$
 $P_{D_2}^O = 60 \text{ mm}$

Table 6h (Pt)

Hyperfine Distribution (%) of C_3H_5D and $C_3H_4D_2$

No.	Conv. (%)	propylene- d_1			propylene- d_2		
		c-1- d_1	t-1- d_1	2- d_1	1,1- d_2	t-1,2- d_2	c-1,2- d_2
25	30	7.7 ± 0.3	44.7 ± 3.4	47.6 ± 3.4	3.2 ± 0.2	13.8 ± 0.7	83.0 ± 0.6
24	50	8.5 ± 0.4	42.7 ± 4.8	48.8 ± 4.5	3.4 ± 0.2	14.8 ± 1.3	81.8 ± 1.0
23	70	8.6 ± 0.5	43.3 ± 5.6	48.1 ± 6.2	2.8 ± 0.2	16.0 ± 0.8	81.2 ± 0.6

$$P_{C_3H_4}^O = 30 \text{ mm}, \quad P_{D_2}^O = 60 \text{ mm}, \quad \text{Reaction temperature} = 25^\circ$$

4) Rhodium catalyst. All possible deuteropropylenes were produced during the reaction over rhodium-black catalyst, as shown in Table 7f. Moreover the exchange reaction of methylacetylene with deuterium occurred rapidly, and methylacetylene- d_1 was produced in large quantities. The mean number of deuterium in propylene increased as the reaction proceeded. This increase of the mean deuterium number in propylene would be due to the increase of the fraction of methylacetylene- d_1 .

The reaction of methylacetylene with non-equilibrated mixture of H_2 and D_2 was investigated. The fine distribution of deuteropropylene obtained by this reaction is shown in the lowest line of Table 7f. The distribution shows clearly that scrambling of hydrogen and deuterium takes place on the surface, because if not, the yield of propylene- d_1 will be smaller, while that of propylene- d_2 will be greater than the observed value.

Table 7h indicates that all possible isomers of propylene- d_2 were produced, so that appreciable amount of deuterium atoms substituted hydrogen atoms in the methyl group.

The yield of cis-1,2- d_2 decreased as the reaction proceeded, while 1,1- d_2 and trans-1,2- d_2 increased.

Table 7f

Rhodium-Catalyzed Reaction (25°C)

Fine Distribution (%) of Deuteromethylacetylene and Deuteropropylene

No.	Conv. (%)	Methylacetylene				Propylene							$\frac{\Phi}{100}$
		d ₀	d ₁	d ₂	d ₃ , d ₄	d ₀	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆	
49	30	81.8	18.2	—	—	3.4	21.2	52.3	19.3	1.7	1.2	0.9	2.0 ₂
51	50	62.9	37.1	—	—	3.4	20.5	47.9	24.5	1.9	1.0	0.8	2.0 ₇
50	70	57.3	42.4	0.3	—	3.1	19.6	47.7	25.7	2.1	1.1	0.7	2.1 ₀
a)													
(r.d. in 3H)		(62.9)	(31.5)	(5.3)	(0.3)								
(r.d. in 4H)		(63.3)	(30.7)	(5.6)	(0.4)								
H ₃ + D ₂ + C ₃ H ₄													
53	30	30.1	33.1	27.1	(mm)	44.2	40.4	13.5	1.9	—	—	—	0.7 ₃

$P_{C_3H_4}^O = 30$ mm, $P_{D_2}^O = 60$ mm, except No. 53

a) Calculated distribution of deuteromethylacetylene (No. 50) by random distribution law;

$$d_i = a C_i (1 - \psi)^{a-i} (\psi)^i, \quad \psi = \frac{1}{a} \cdot \frac{1}{100} \sum i \cdot d_i,$$

where a is the number of exchangeable hydrogen atoms and $0 \leq i \leq 4$.

Table 7h (Rh)

Hyperfine Distribution (%) of C_3H_5D and $C_3H_4D_2$

No.	Conv. (%)	Propylene- d_1			
		t-1- d_1	c-1- d_1	2- d_1	3- d_1
50	70	17.4 ± 0.5	37.0 ± 2.0	42.8 ± 2.7	2.8 ± 0.5

		Propylene- d_2					
		1,1- d_2	t-1,2- d_2	c-1,2- d_2	1,3- d_2	2,3- d_2	3,3- d_2
49	30	17.7 ± 1.9	19.1 ± 0.6	58.6 ± 1.4	1.5 ± 0.4	1.4 ± 0.2	1.7 ± 0.1
50	70	20.8 ± 1.2	21.2 ± 3.0	53.3 ± 1.8	1.4 ± 0.3	1.5 ± 0.2	1.8 ± 0.3

$$P_{C_3H_4}^O = 30 \text{ mm}, \quad P_{D_2}^O = 60 \text{ mm}, \quad 25^\circ$$

5) Iridium catalyst. All possible deuteropropylenes were produced over iridium-black catalyst as shown in Table 8f. The yield of propylene-d₂ and the mean number of deuterium in propylene decreased as the reaction proceeded, while the yield of propylene-d₁ increased. The exchange degree of methylacetylene with deuterium was very small and increased gradually. The return of hydrogen to the gas phase was larger than those observed over Ni, Pd and Pt catalysts.

In order to investigate the effect of initially added propylene upon the fine distribution of deuteropropane, the reaction with the mixture which consisted of methylacetylene (30 mm), propylene (26 mm) and deuterium (60 mm) was carried out at 25°. The result of this reaction (No. 35) is shown in the lowest line of Table 8f, together with the result of No. 36, in which the standard mixture was used. As is seen from these results, initially added propylene did not significantly affect the fine distribution of deuteropropane.

Of the propylene-d₂ isomers, cis-1,2-d₂ was the major product, and the isomers in which the methyl group was substituted by deuterium were detected in a relatively large amount. The yield of cis-1,2-d₂ decreased as the reaction proceeded, while 1,1-d₂ and trans-1,2-d₂ increased.

Table 8f

Iridium-Catalyzed Reaction (25°)

Fine Distribution of Deuteromethylacetylene and Deuteropropylene

No.	Conv. (%)	Methylacetylene			Propylene							$\frac{\Phi}{100}$
		d ₀	d ₁	$\sum d_2$	d ₀	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆	
31	30	99.2	0.8	—	1.5	13.4	57.1	20.4	3.0	2.5	2.1	2.2 ₆
30	50	98.8	1.2	—	2.7	13.5	56.7	20.2	2.7	2.3	1.9	2.2 ₁
32	70	98.3	1.7	—	1.8	16.0	55.0	20.4	2.8	2.4	1.6	2.2 ₀
33	85	97.7	2.3	—	2.2	17.3	53.4	20.6	2.9	2.1	1.5	2.1 ₇

No.	P ^O C ₃ H ₆ (mm)	Conv. (%)	Propane									
			d ₀	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆	d ₇	d ₈	
35	26	50	—	1.8	5.4	11.1	33.8	34.4	4.6	5.3	3.6	
36	0	50	—	1.5	2.4	8.2	34.8	37.8	5.4	6.1	3.8	

$$P_{C_3H_4}^O = 30 \text{ mm}, \quad P_{D_2}^O = 60 \text{ mm}.$$

Table 8h (Ir)

Hyperfine Distribution (%) of C_3H_5D and $C_3H_4D_2$

No.	Conv. (%)	Propylene-d ₁			
		c-1-d ₁	t-1-d ₁	2-d ₁	3-d ₁
30	50	7.0 ± 0.3	46.2 ± 2.7	45.5 ± 4.1	1.4 ± 0.4
32	70	9.4 ± 0.3	45.8 ± 2.0	43.7 ± 3.8	1.1 ± 0.3
33	85	9.6 ± 0.3	45.2 ± 2.4	43.5 ± 2.2	1.6 ± 0.3

		Propylene-d ₂					
		1,1-d ₂	t-1,2-d ₂	c-1,2-d ₂	1,3-d ₂	2,3-d ₂	3,3-d ₂
30	50	7.1 ± 0.3	8.5 ± 0.4	82.7 ± 0.8	0.4 ± 0.1	0.9 ± 0.2	0.5 ± 0.1
32	70	9.1 ± 0.6	10.4 ± 0.4	78.0 ± 0.9	0.6 ± 0.2	1.0 ± 0.2	0.9 ± 0.1
33	85	10.9 ± 0.9	11.8 ± 1.1	74.9 ± 1.4	0.7 ± 0.1	1.0 ± 0.2	0.7 ± 0.2

$$P_{C_3H_4}^O = 30 \text{ mm}, \quad P_{D_2}^O = 60 \text{ mm}, \quad 25^\circ$$

6) Ruthenium catalyst. Ruthenium was investigated as one of the Group VIII metals having the closed-packed hexagonal structure, while the above-mentioned five metals have a face-centered cubic structure.

The fine distribution of deuteropropylene obtained over Ru-black was similar to that obtained over Rh- and Ir-black catalysts; i.e., all possible deuterated propylenes were formed and propylene-d₂ was the major product.

The mean number of deuterium atoms in propylene was larger than those obtained over the other five metals, and it decreased as the reaction proceeded.

Table 9h indicates that the methyl group was substituted by deuterium atoms in an appreciable amount. The major product was propylene-cis-1,2-d₂, but it decreased as the reaction proceeded.

Over Ru-black catalyst allene was produced during the hydrogenation. The fine distribution of deuterioallene was also determined by mass spectrometry and is shown in Table 9f. Fine distribution of deuterioallene was similar to that of deuteromethylacetylene, i.e., allene-d₀ is dominant.

Table 9f

Ruthenium-Catalyzed Reaction (25°)

Fine Distribution of Deuteromethylacetylene and Deuteropropylene

No.	Conv. (%)	Methylacetylene			Propylene							$\frac{\Phi}{100}$
		d ₀	d ₁	$\geq d_2$	d ₀	d ₁	d ₂	d ₃	d ₄	d ₅	d ₆	
57	30	94. ₁	5. ₉	—	1. ₇	10. ₇	46. ₇	33. ₀	3. ₃	2. ₄	2. ₂	2.4 ₂
55	50	85. ₁	14. ₉	—	1. ₈	11. ₉	45. ₂	33. ₁	3. ₃	2. ₆	2. ₁	2.4 ₀
56	70	87. ₂	12. ₈	—	1. ₇	12. ₈	45. ₄	32. ₈	3. ₂	2. ₂	1. ₉	2.3 ₇
		Allene-d ₀	d ₁	$\geq d_2$								
		88. ₈	11. ₂	—								

$P_{C_3H_4}^O = 30 \text{ mm},$
 $P_{D_2}^O = 60 \text{ mm}.$

Table 9h (Ru)

Hyperfine Distribution (%) of C_3H_5D and $C_3H_4D_2$

No.	Conv. (%)	Propylene- d_1			
		c-1- d_1	t-1- d_1	2- d_1	3- d_1
56	70	16.2 ± 0.9	42.8 ± 6.0	37.7 ± 3.6	3.3 ± 0.6

		Propylene- d_2					
		1,1- d_2	t-1,2- d_2	c-1,2- d_2	1,3- d_2	2,3- d_2	3,3- d_2
57	30	16.9 ± 2.3	15.9 ± 1.6	63.4 ± 2.2	1.4 ± 0.4	1.6 ± 0.3	0.8 ± 0.3
56	70	19.8 ± 1.3	17.4 ± 1.6	58.2 ± 1.7	1.3 ± 0.6	2.7 ± 0.5	0.6 ± 0.1

$$P_{C_3H_4}^O = 30 \text{ mm}, \quad P_{D_2}^O = 60 \text{ mm}, \quad 25^\circ$$

Table 10

Percentage Distribution of ^{13}C -methylacetylene and ^{13}C -propylene
Produced by the Reaction of $^{13}\text{CH}_3\text{-C}\equiv\text{CH}+\text{H}_2$ at 25° on Nickel powder.

Species	Before the reaction	After the reaction
Methylacetylene		
$^*\text{CH}_3\text{-C}\equiv\text{CH}$	1.1 ± 0.2	1.2 ± 0.2
$\text{CH}_3\text{-}^*\text{C}\equiv\text{CH}$	1.1 ± 0.2	1.1 ± 0.2
$\text{CH}_3\text{-C}\equiv^*\text{CH}$	97.8 ± 0.3	97.8 ± 0.3
Propylene		
$^*\text{CH}_3\text{-CH=CH}_2$		1.7 ± 0.1
$\text{CH}_3\text{-}^*\text{CH=CH}_2$		1.0 ± 0.1
$\text{CH}_3\text{-CH=}^*\text{CH}_2$		97.3 ± 0.2

Part B Isomerization

As stated in the previous section (III-A), allene ($\text{CH}_2=\text{C}=\text{CH}_2$) which is an isomer of methylacetylene was found to appear during the hydrogenation of methylacetylene over ruthenium-black, but not over the other metal catalysts. Isomerization of methylacetylene to allene over Group VIII metals was not reported either in the presence or absence of hydrogen until now.³⁾

From the mechanistic viewpoint, it is very important to study that allene was producible whether through a process of the hydrogenation or not. In order to elucidate this problem, the isomerization between methylacetylene and allene was studied mainly over ruthenium-black catalysts in the absence of hydrogen.

B-1. Catalytic activity of each metal.

To begin with, the catalytic activity of each metal for the isomerization was compared. Amount of the metal catalyst and volume of the reaction vessel in each run were the same as applied for the study of hydrogenation of methylacetylene (See Table 1). Methylacetylene (30 mm) alone was introduced into the reaction vessel, and was allowed to stand for twenty days at 25° , except over ruthenium-black, because all these catalysts exhibited very low activity for the isomerization.

On the other hand, ruthenium-black was very active, so that the composition of methylacetylene and allene was analyzed for each one hour.

Catalytic activity of each metal for the isomerization is represented by the initial rate of allene formation per unit surface area and is listed in Table 11. In the right column of the table, activity for the hydrogenation is also summarized for reference.

As shown in Table 11, ruthenium-black exhibited a very high activity for the isomerization. Its activity was approximately five hundred or more times the activities of the other metals. The rate of the isomerization and that of hydrogenation were of comparable order over ruthenium-black. Therefore, allene could be detected during the hydrogenation. Over the other metals, however, the hydrogenation was faster in rate by about five or more orders of magnitude than the isomerization.

B-2. Isomerization over ruthenium-black

The catalyzed isomerization of methylacetylene to allene was kinetically studied in more details over ruthenium-black, using the apparatus shown in Fig. 2.

The allene formation always reached a stationary value; e.g., when the reaction was started from 29.8 mm

Table 11

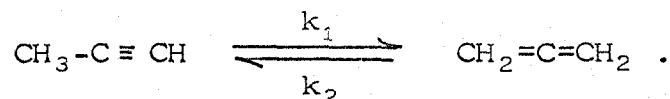
Catalytic Activity for Methylacetylene-Allene Isomerization

Catalyst	Activity for allene formation from methylacetylene ^{*)} (mol/m ² -cat. hr)	Activity for hydrogenation ^{**)} (mol/m ² -cat. hr)
Ni	—	8.4×10^{-4}
Pd	3.5×10^{-9}	7.8×10^{-3}
Pt	$\leq 10^{-9}$	9.6×10^{-4}
Rh	3.5×10^{-9}	1.2×10^{-3}
Ir	$\leq 10^{-9}$	6.6×10^{-4}
Ru	1.8×10^{-6}	6.0×10^{-5}

*) Initial partial pressure of methylacetylene was
30 mm.

**) This value was represented by the initial rate of
methylacetylene removal during the hydrogenation.

of methylacetylene, the produced allene increased to 2.9₅ mm asymptotically after three days. This value may be establishment of the equilibrium due to the reversed reaction ; e.g.,



If so, decrease of methylacetylene must obey the first-order rate shown by eq.(1)

$$k = k_1 + k_2 = \frac{1}{t} \ln \frac{x_e}{x_e - x} \quad (1)$$

where x is the concentration of allene at time t and x_e its equilibrium value. Fig.7a shows a plot of the rate of the isomerization, which was started from 29.8 mm of methylacetylene, vs. time.

The initial rate of allene formation was independent of the initial pressure of methylacetylene as shown in Fig. 7b, where partial pressure of the produced allene was plotted against time. Equilibrium concentrations of both compounds are shown below in comparison with their theoretical values (cf. discussion).

	$\text{CH}_3\text{-C}\equiv\text{CH}$	$\text{CH}_2=\text{C}=\text{CH}_2$
obs.	90.1 %	9.9 %
theor.	96.5 %	3.5 %

Error of the experimental value was less than 0.2 %.

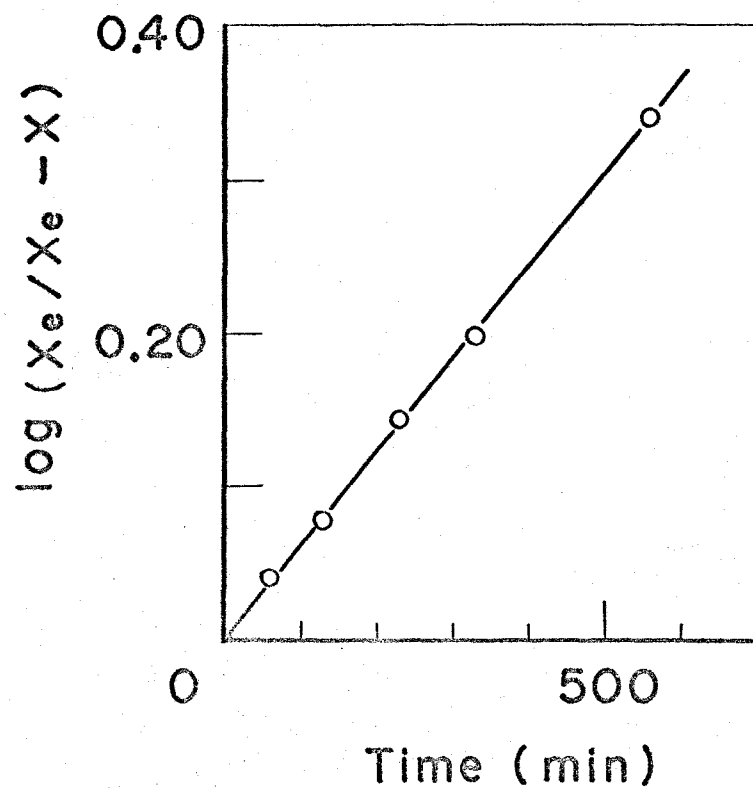


Fig. 7 (a). First order rate plots for the isomerization of 29.8 mm of methylacetylene over Ru-black at 25°.

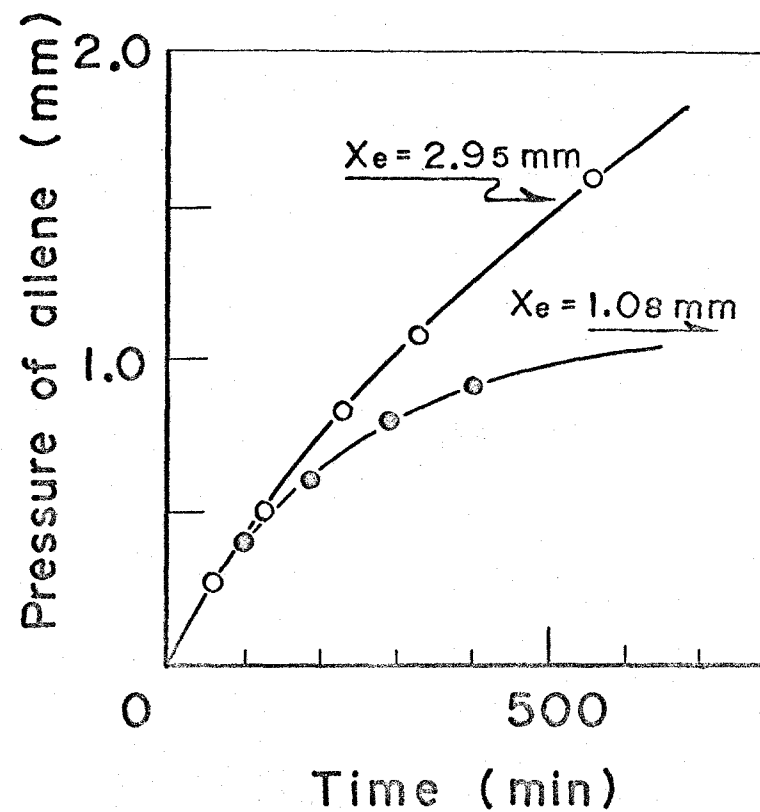


Fig. 7 (b). Time-course of the allene formation from 29.8 mm or 10.9 mm of methylacetylene over Ru-black at 25°.

B-3. Effect of acetylene to the isomerization

The effect of initially added acetylene upon the rate of the isomerization was examined at 25° . The initial partial pressure of methylacetylene was fixed at about 11 mm and that of acetylene was varied in the range 1.1 — 11.0 mm. Fig. 8 shows the dependence of the initial rate of allene formation upon the initial acetylene pressure. Addition of a small amount of acetylene decreased markedly the rate of allene formation. The rate observed with equimolal mixture of methylacetylene and acetylene was approximately $1/35$ of the rate observed in the absence of acetylene.

The effect of deuterium upon the isomerization was also examined by using two kinds of deuterium-methylacetylene mixture ($P_{C_3H_4}^{\circ} / P_{D_2}^{\circ} = 1$ and $1/2$), where the initial methylacetylene pressure was fixed within 29.4 — 29.8 mm. The rate of allene formation was decreased linearly as the initial deuterium pressure was increased as shown in Fig. 9.

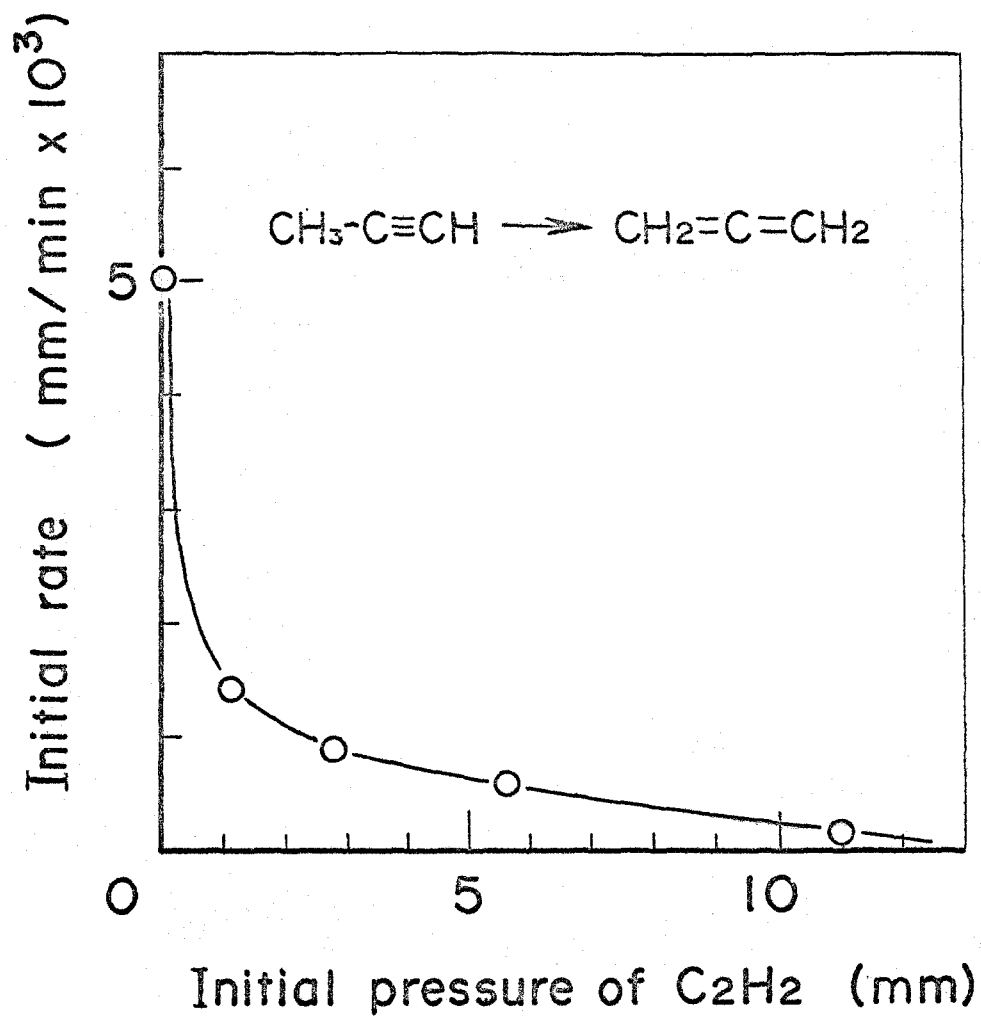


Fig. 8. Dependence of isomerization rate of methylacetylene upon the initial added acetylene, over Ru-black at 25° .

$$(P_{\text{C}_3\text{H}_4})^0 = 11.0 \text{ mm.}$$

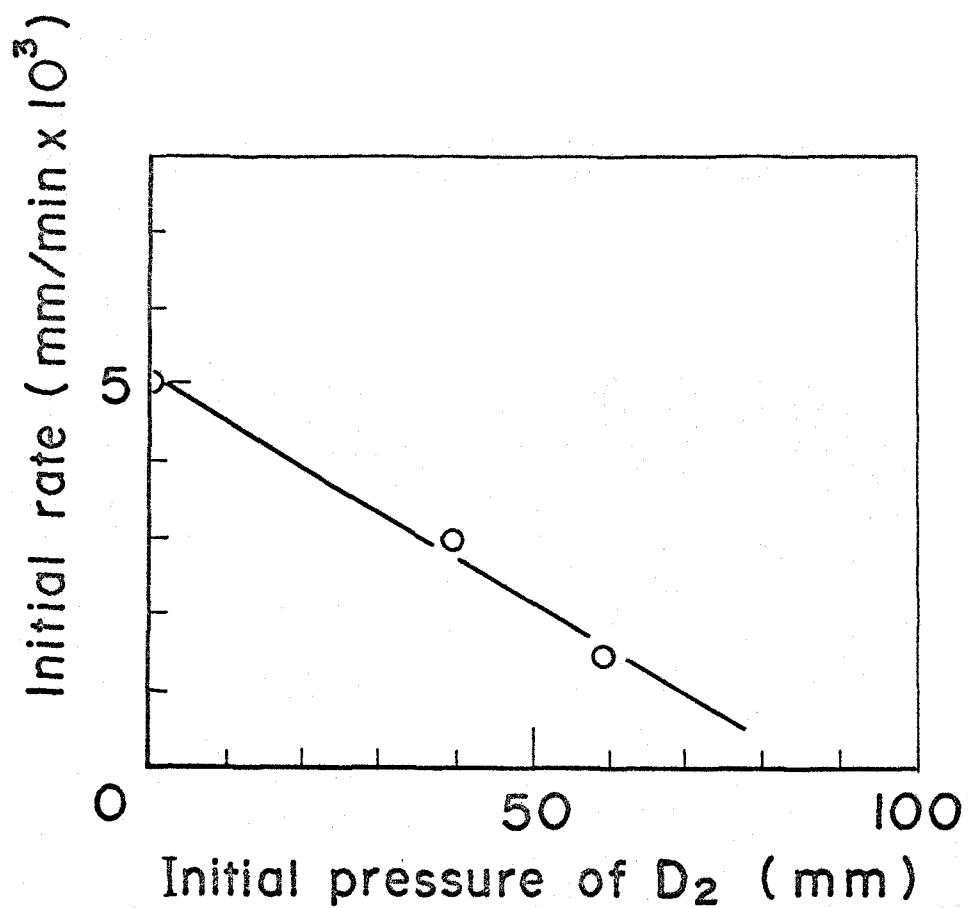


Fig. 9. Dependence of isomerization rate of methylacetylene upon the initial added deuterium, over Ru-black at 25°.

$$(P_{\text{C}_3\text{H}_4})^0 = 29.4 \text{ mm} \sim 29.8 \text{ mm}.$$

B-4. Isomerization accompanied by deuterium exchange

Dideuteroacetylene was selected as the reagent which can provide deuterium atoms to the isomerization without bringing about the hydrogenation. An equimolal mixture of dideuteroacetylene (11.0 mm) and methylacetylene (11.0 mm) was allowed to stand for three days at 25°. The produced allene amounted to five percent of the initial amount of methylacetylene.

Deuterium distributions in acetylene, allene and methylacetylene were determined by the mass spectrometry, and they are summarized in Table 12. In the table, values in parentheses denote the distributions calculated on the basis of the random-distribution law, eq. (2).

$$\psi = \frac{1}{a} \cdot \frac{1}{100} \sum_i i(d_i)_{\text{obs}} \quad (2)$$

$$(d_i)_{\text{calc}} = {}_a C_i (1 - \psi)^{a-i} (\psi)^i \times 100$$

where a is the number of hydrogen atoms equivalent for deuterium exchange and d_i the composition of d_i species in percent. Consequently, ψ denotes the degree of deuteration.

As shown in Table 12, a large amount of deuterium atoms was transferred from acetylene to methylacetylene and allene. The fine distribution of deuterio-allene

Table 12

Fine Distribution of Deuterium in the Products after the Reaction of
 $\text{CH}_3 - \text{C} \equiv \text{CH} + \text{C}_2\text{D}_2$ (1 : 1) over Ruthenium Black at 25° .

Materials	d_0	d_1	d_2	d_3	d_4	$\frac{\Phi}{100}$	Composition (mm)
Before the reaction							
Acetylene	—	1.5	98.4	—	—	1.9 ₈	11.0
Methylacetylene	100.0	—	—	—	—	0.0	11.0
After the reaction for 3 days							
Acetylene	11.8	44.5	43.7	—	—	1.3 ₂	11.0
(r.d.* in 2H)	(11.6)	(44.9)	(43.6)	—	—	—	—
Allene	33.8	62.1	4.1	—	—	0.7 ₀	0.6
(r.d. in 2H)	(42.1)	(45.6)	(12.3)	(—)	(—)	—	—
(r.d. in 4H)	(46.1)	(39.4)	(12.6)	(1.8)	(0.1)	—	—
Methylacetylene	36.0	63.3	0.7	—	—	0.6 ₅	10.4
(r.d. in 3H)	(48.2)	(39.8)	(11.0)	(1.0)	(—)	—	—
(r.d. in 4H)	(49.3)	(38.1)	(11.0)	(1.4)	(0.2)	—	—

*) Calculated value on the basis of the random-distribution law, $d_i = {}_aC_i (\psi)^i (1 - \psi)^{a-i}$,
 e.g., 2H denotes $a = 2$.

was very similar in shape to that of deuteromethylacetylene. This is analogous to the result of the reaction of deuterium and methylacetylene (See Table 9f).

B-5. Isomerization and hydrogenation of allene

The isomerization of allene to methylacetylene was also examined kinetically over ruthenium-black at 25°. The rate was faster than that of its reversed reaction, as expected from the fact that the isomerization equilibrium shifts to the side of methylacetylene. The rate of methylacetylene formation was independent of the initial allene pressure, which was varied from 29.5 mm to 5.4 mm.

The methylacetylene formation vs. time is shown by a dotted line in Fig. 10. This isomerization was started from 29.5 mm of allene and did not obey the first order rate represented by eq. (1). The equilibrium concentration of each component was the same as obtained by the isomerization started from methylacetylene, i.e., 90.1 % of methylacetylene and 9.9 % of allene.

Hydrogenation of allene was carried out with the mixture which consisted of 28.8 mm of allene and 57.7 mm of deuterium. Time-course of the partial pressure of each hydrocarbon is shown by a full line in Fig. 10.

In the course of the reaction, methylacetylene was produced in a large amount, increasing as the reaction proceeded. However, the methylacetylene formation during the reaction was slower than that in the absence of deuterium.

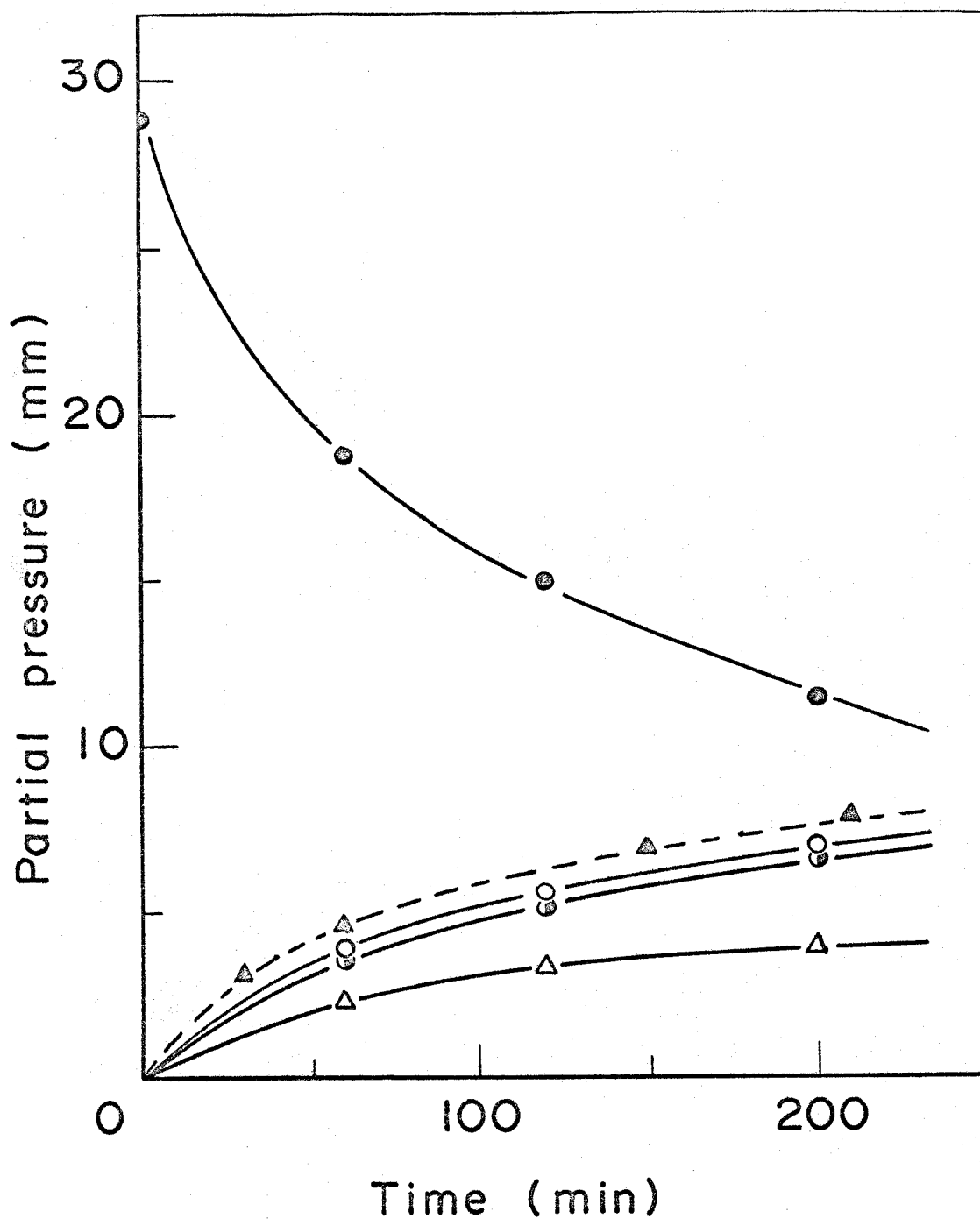


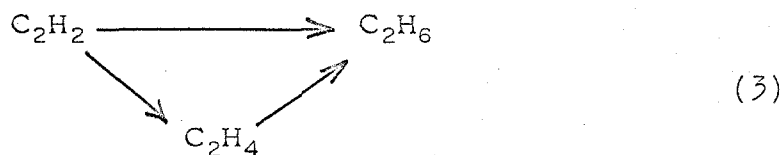
Fig. 10. Partial pressure of each hydrocarbon against time curve for the hydrogenation of allene $\text{CH}_2=\text{C}=\text{CH}_2$ (28.8 mm) with deuterium (57.7 mm) over Ru-black at 25° .

●, allene; ○, propylene; ◐, propane
 Δ, methylacetylene;
 --Δ--Δ--, partial pressure of methylacetylene produced in the absence of deuterium.

Chapter IV DISCUSSION

1. Hydrogenation.

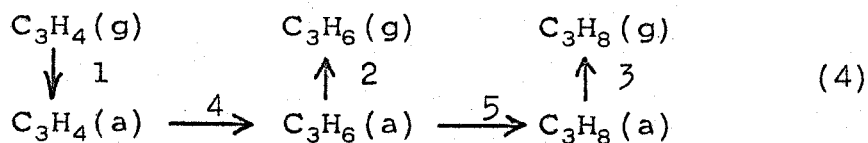
1) Reaction curves and selectivity. Consecutive reactions, where a reactant is converted into an intermediate compound which may further react and form a final product, occur often in heterogeneously catalyzed reactions. The catalytic hydrogenation of acetylenic compounds clearly belongs to such a system. Several approaches have been made to the theoretical treatment of a consecutive reaction and the selectivity for the formation of the intermediate compound has been discussed.¹⁹⁾ Bond et al.²⁾ have studied the catalytic hydrogenation of acetylene, and concluded that the scheme of this reaction could be represented generally by eq. (3)



In the present investigation where the reaction of methylacetylene with deuterium was carried out, propylene and propane were produced simultaneously. Moreover, the selectivity for propylene formation (S) remained constant during the first stage of the reaction over all the six metals. These findings suggest that the formation of propane is due to the hydrogenation

of the formed propylene adsorbed on the surface from methylacetylene and not by readsorption of propylene from the gaseous phase. This conclusion is decisively supported by the results that the initial addition of propylene did not affect not only the hydrogenation rate, but also the fine distribution of deuteropropane (see Table 8f) even over iridium-black, which exhibited the lowest selectivity of the six metal catalysts.

Thus the propylene, which was produced by the reaction and was desorbed, could not be readsorbed and could not enter into the reactive layer at the surface in the first stage of the reaction. It is considered that methylacetylene was adsorbed more strongly than propylene and propane on the metal surface, judging from the initial heat of adsorption of acetylene (67 Kcal/mol), and that of ethylene (58 Kcal/mol) on nickel surface.²⁰⁾ The readsorption of propylene which corresponds to $C_2H_4 \rightarrow C_2H_6$ in eq. (3) might be prohibited by the strongly adsorbed methylacetylene. The scheme in the first stage of the reaction may be written simply by eq. (4).



In this scheme, the backward reaction of step 2 is

ruled out by the reasons above mentioned, and that of step 3 is also ruled out because of the weaker adsorption of propane, compared with propylene on the metal surface.²⁰⁾

The adsorbed propylene $C_3H_6(a)$ undergoes either desorption (step 2) or further hydrogenation (step 5), and here the paths to the formation of propylene and propane become independent. The backward reaction of step 1,4,5 and details of the mechanism are discussed in the next section.

After the acceleration point, the dominant reaction changed from the hydrogenation of methylacetylene to the further hydrogenation of propylene to propane. This change was clearly shown by the time-dependence of the selectivity for propylene formation over ruthenium and palladium (see Fig. 6). Thus readsorption of propylene in the gaseous phase occurs in the second stage of the reaction. These facts show that both reactions occur on the same kind of sites, and that methylacetylene and propylene are adsorbed competitively on the catalyst surface. Methylacetylene was found to be superior to propylene in adsorption until the acceleration point, but not in the second stage. Mann and Khulbe^{14-b)} suggested that the selectivity for propylene formation might be governed by the difference in the adsorbabilities of methylacetylene and propylene

on the catalyst surface and not to the difference in the rate of hydrogenation reaction, i.e., the catalyst on which the difference of their adsorbabilities is larger would exhibit higher selectivity.

This difference can be expressed by the minimum value of propylene : methylacetylene ratio, which is necessary to secure the entrance of propylene into the reactive layer covered with methylacetylene and to enable the propylene hydrogenation to be detectable. Determination of this ratio requires full analysis to be carried out, but this ratio may be represented for convenience by the ratio of the partial pressure of remaining methylacetylene to that of produced propylene at the acceleration point. The acceleration point is the critical point where readsorption of propylene is allowed. Therefore, the ratio obtained by this method may estimate the difference of their adsorbabilities with a reasonable certainty.

Fortunately, side reactions such as polymerization did not occur in the present investigation, and the selectivity for propylene formation was constant in the first stage of the reaction over all the catalysts. The partial pressure of each hydrocarbon at the acceleration point is easily calculated by using the value of selectivity and that of pressure fall at the

acceleration point. Calculated values are summarized in Table 13. In this Table, $(C_3H_6/C_3H_4)_a$ denotes the partial pressure ratio of propylene to methylacetylene at the acceleration point. The ratio $(C_3H_6/C_3H_4)_a$ decreased in the following sequence.

$$Rh > Pd > Ni \geq Pt$$

The difference of the adsorbabilities of methylacetylene and propylene may tend to decrease in this order.

High ratios were observed over ruthenium and iridium, but the absolute amounts of the produced propylene were so small that they could not be compared with the values obtained over the other catalysts.

If the selectivity for propylene formation is governed only by the difference of adsorbability as suggested by Mann and Khulbe, the order of selectivity will be the above sequence. However, the observed order was

$$Pd > Pt > Rh > Ni > Ru > Ir.$$

In the hydrogenation of acetylene over Pd, Pt, Ni, Ir and Rh supported by alumina, the ratio $(C_2H_4/C_2H_2)_a$ at the acceleration point was the highest over Rh, but Rh did not exhibit the highest selectivity for ethylene formation of the five catalysts.²¹⁾ Thus the difference of their adsorbabilities is not the only factor to determine the selectivity for propylene

Table 13

Composition of Hydrocarbons at the Acceleration Point

Cat.	P_{MA}^O (mm)	S	$-\Delta P_a$ (mm)	Partial pressure (mm)			$\left(\frac{C_3H_6}{C_3H_4}\right)_a$ *)
				C_3H_4	C_3H_6	C_3H_8	
Ni	29.8	0.76	34.3	2.2	21.0	6.6	9.5
Pd	30.0	0.98	29.1	0.9	28.4	0.7	31.6
Pt	30.2	0.93	29.1	3.0	25.3	1.9	8.4
Rh	30.1	0.86	34.0	0.3	25.6	4.2	85.3
Ir	30.2	0.28	51.4	0.2	8.4	21.6	42.0
Ru	30.1	0.45	46.5	0.1	13.5	16.5	13.5

*) The partial pressure ratio of propylene to methylacetylene at the acceleration point.

formation, and ratio of the rate of step 2 to that of step 5 in eq.(4) must be considered as one of the factors.

2) Activity. The catalytic activity, which is represented by the rate of methylacetylene decrease per unit surface area of each metal, can be summarized by the following order:



The activity of palladium was approximately one hundred times more than that of ruthenium. Similar activity order was already reported by Bond et al.²²⁾ for the hydrogenation of acetylene over evaporated metal films, where Ir and Ru was not included. The activity order for methylacetylene hydrogenation was determined by Mann and Khulbe, but they used the values per unit weight of each metal to compare the activities with each other. Therefore, their result cannot be compared with the present one.

The rates of pressure fall during the course of the first stage of the reaction was proportional to the first power of the remaining hydrogen pressure over all the catalysts, as shown in Fig. 5. This fact is concordant with the rate expression for the methylacetylene hydrogenation given by

$$-d(P_{\text{C}_3\text{H}_4})/dt = k \cdot (P_{\text{H}_2})^{1.0} \cdot (P_{\text{C}_3\text{H}_4})^0, \quad (5)$$

which is generally proposed by the recent kinetic studies of the reaction over Group VIII metal catalysts.^{13, 14)} The surface was, therefore, mostly covered with adsorbed methylacetylene until the acceleration point, whereas hydrogen was comparatively weakly adsorbed, its surface coverage being correspondingly low. In other words, the rate decreased during the first stage of the reaction as the concentration of adsorbed hydrogen diminished, accompanying the decrease of the partial pressure of hydrogen.

2. Isomerization

1) Equilibrium concentration. Experimentally, equilibrium concentrations of methylacetylene and allene are determined at 25° in Part B of Chapter III where they were summarized. However, they seem to be much different from the theoretical values, which are calculated from their standard free energies, i. e., $G^{\circ}/T = 651.2 \text{ J/mol}\cdot\text{deg}$ for methylacetylene and $678.8 \text{ J/mol}\cdot\text{deg}$ for allene.¹⁸⁾

Such a discrepancy between experiment and theory ^{might} ~~may~~ be obtainable by some irreversible side reaction accompanied by the isomerization. In the present investigation, however, any side reaction was not observed markedly. As a possible product of side reactions, propylene and/or propane which must be produced by the self-hydrogenation of methylacetylene was only detected, but its amount was less than 0.2 percent of the initial amount of methylacetylene. Moreover, formation of polymers was not detected by gas chromatography. Such a negligibly small extent of side reactions would not affect the equilibrium composition significantly. The above experimental equilibrium values, therefore, may be intrinsic, so that redetermination of the free energies of both compounds might be necessary.

2) Kinetics of the isomerization. The fact that a first-order rate was observed in the isomerization from methylacetylene but not in the reaction from allene indicates adsorption of methylacetylene to be stronger than that of allene during the isomerization. When the reaction is started from methylacetylene, the fraction of allene can not increase more than ten percent of the total amount. The surface coverage of allene is, therefore, considered to be also less than ten percent ($\theta \leq 0.1$), so that the produced allene may not prohibit significantly the reaction. This is the reason why the first order rate was observed in a long range of the reaction from methylacetylene. This conclusion is consistent with the study of Bond et al.,²²⁾ who estimated the surface coverages of methylacetylene and allene over nickel catalyst, by measuring the rate of hydrogenation of the binary mixture (1 : 1) and by determining their specific rates of both reactants. The isomerization between allene and methylacetylene was not reported on this catalyst. According to this study, methylacetylene was more strongly adsorbed than allene, and their surface coverages were 0.76 for methylacetylene and 0.24 for allene, respectively. Thus the prohibition of the produced allene to the reaction by its adsorption becomes less probable.

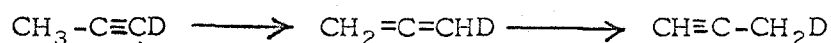
On the other hand, it is expected that the reaction from allene is affected by the increase of the produced methylacetylene. In the initial stage of the reaction, the catalyst surface is covered completely with allene, and the reaction from allene is faster than that from methylacetylene, judging from the fact that the isomerization equilibrium shifts to the side of methylacetylene. As the reaction proceeds, however, the surface coverage of methylacetylene increases more rapidly than expected from the composition in the gaseous phase by the strong adsorption of methylacetylene. Consequently, the surface coverage of allene decreases rapidly, so that the methylacetylene formation may not obey the first-order rate.

3) Effect of adsorption and desorption processes.

Initial rate of the isomerization was not affected by the initial pressure of a reactant, methylacetylene or allene. This result indicates that the surface of ruthenium-black catalyst is almost completely covered with the reactant. Under such a condition, it is often observed that the rate-determining step of the reaction exists in the desorption of an isomerization product. In the present investigation, however, the rate-determining step is considered to exist not in the desorption process, but in the surface reaction, judging

form the fine distributions of deuteromethylacetylene and deuterioallene produced by the reaction of light methylacetylene (C_3H_4) with di-deuteroacetylene (C_2D_2), as will be discussed.

If the rate-determining step exists in the desorption process, the surface reaction would be in quasi-equilibrium, and methyl hydrogens and acetylenic hydrogen of methylacetylene would be equivalent for deuterium exchange as shown by the following scheme.



Consequently, the fine distribution of deuteromethylacetylene and deuterioallene must be consistent with the random distribution assuming all the four hydrogens to be equivalent for deuterium exchange.

In practice, however, the fine distribution of deuteromethylacetylene is markedly different from the two kinds of calculated distributions, as shown by r.d. in 3H and r.d. in 4H in Table 12. In the former case three hydrogen atoms of methyl position are assumed to be substituted by deuterium, while in the latter case four hydrogen atoms to be equivalent. This result indicates that almost all the methylacetylene- d_1 may be $CH_3-C\equiv CD$. Deuterium atoms in the produced deuterioallene are also considered to localize at one of the hydrogen positions, judging from the difference between

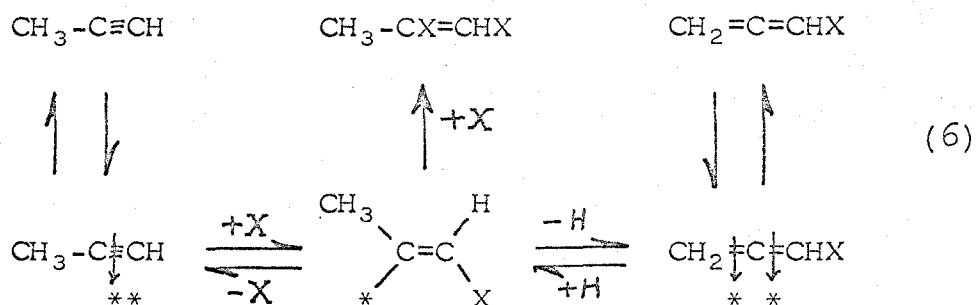
the observed distribution and two kinds of calculated distributions as shown by r.d. in 2H and r.d. in 4H in Table 12.

From these findings, the above mentioned conclusion is verified. Furthermore, this conclusion can be supported by the fact that the least amount of acetylene decreased the isomerization rate markedly.

4) Mechanism of isomerization. Table 9f shows that in the presence of gaseous deuterium, the fine distribution of deuterioallene was also similar in shape to that of deuteromethylacetylene, as well as in the reaction of methylacetylene with di-deuteroacetylene. This indicates that the mechanism of the isomerization must be considered so as to keep the mutual distribution of deuterium between two compounds equal.

Wells et al.²³⁾ detected the appearance of a trace of methylallene ($\text{CH}_3\text{-CH=CH}_2$) during the hydrogenation of dimethylacetylene ($\text{CH}_3\text{-C}\equiv\text{C-CH}_3$) over alumina-supported rhodium and iridium catalysts. Based on this finding, they related the formation of methylallene to that of 1-butene which was produced by the hydrogenation of dimethylacetylene, and they proposed the mechanism, i.e., adsorbed methylallene is produced via a half-hydrogenated state of dimethylacetylene and 1-butene is produced by further hydrogenation of the adsorbed

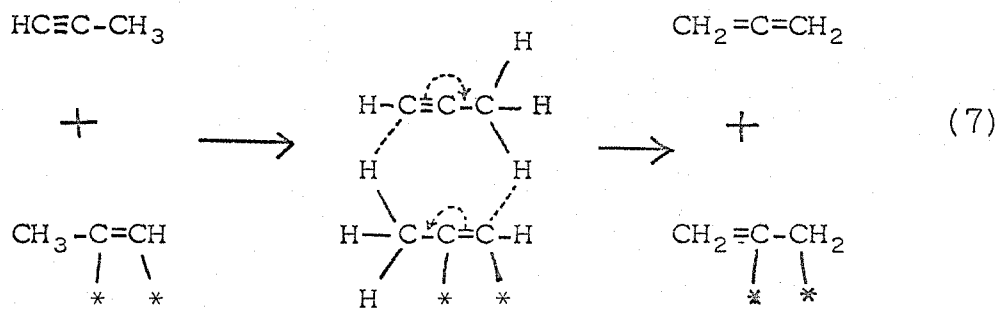
methylallene. If the above mechanism is assumed also to be valid in the hydrogenation of methylacetylene, the corresponding scheme, Eq.(6), can be given, where X is the surface hydrogen atom (H or D).



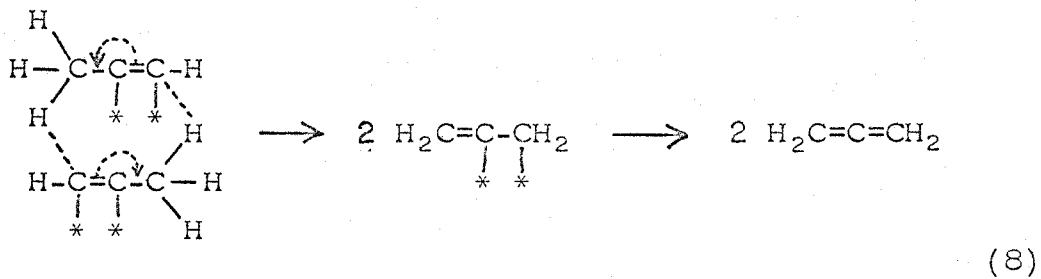
The isomerization of methylacetylene was slower than the hydrogenation as shown in Table 11. In such a case, if allene is produced from methylacetylene through the process of the scheme (6), fine distribution of deuterioallene would be greatly different from that of deuterio-methylacetylene, because of the following reasons. Fine distribution of deuterioallene in gaseous phase would be almost the same as in the adsorbed phase, so that allene-d₁ would be the dominant product, because deuterium is much more adsorbed on the surface than protium during the hydrogenation with deuterium. On the other hand, deuterated methylacetylene does not return to the gaseous phase in anappreciable amount, so that methylacetylene-d₀ would be the most abundant.

Practically, fine distribution of deuterioallene is almost similar to that of deuteromethylacetylene, and allene-d₀ is dominant as shown in Table 9f. Moreover, the isomerization in the absence of hydrogen is very fast, and the rate is not favored by the presence of hydrogen. From these results, it is concluded that the mechanism in eq. (6) may not be adequate for the isomerization of methylacetylene, and that the isomerization occurs independently of the hydrogenation in which a half-hydrogenated methylacetylene may be produced as an intermediate.

Such being the situation, deuterioallene must be produced stepwise, i.e., at first methylacetylene is deuterated and then isomerizes to allene. In order to explain the similar distributions of deuterioallene and deuteromethylacetylene, participation of the surface hydrogen atoms into the isomerization must be ruled out, because it should cause their distributions to be different with each other. Such a situation is fulfilled by an "intramolecular" hydrogen transfer, or by an "intermolecular" hydrogen transfer in which the surface hydrogen is not concerned. Methylacetylene and allene are linear molecules and therefore the intramolecular hydrogen transfer would be very difficult. If the isomerization is due to the latter type, following



Second, two adsorbed methylacetylenes may interact producing two allene molecules;



From the data hitherto obtained; it cannot be determined which mechanism is more probable.

5) High activity of ruthenium-black. Ruthenium-black exhibited a very high activity for the isomerization compared with the other catalysts. This high activity

might be accounted for by its crystal structure, because ruthenium has a closed-packed hexagonal structure and the other metals have a face-centered cubic structure. Such a situation was examined by using cobalt powder, which was prepared by thermal decomposition of cobalt formate at 310° — 330° under vacuum followed by reduction with hydrogen at the same temperature. Under the preparation condition, β -phase (closed-packed hexagonal structure) is stable. Cobalt powders thus obtained had not high activity for the isomerization, i.e., the rate of allene formation from methylacetylene was about 7×10^{-9} mol/m²-cat. hr. Therefore, high activity of ruthenium may be due to other factors; for example, the electronic structure of ruthenium.

3. Deuterium distribution and hydrogenation mechanism.

The maximum in the fine distribution of deuterio-propylene was always at propylene-d₂, and its yield at 70 % conversion decreased in the order.



Propylene-cis-1,2-d₂ is the most abundant of the propylene-d₂ isomers over all the six metals, and its relative yield in the isomers at 70 % conversion decreased in the following order.



The yield of propylene-cis-1,2-d₂ decreased as the reaction proceeded over iridium, ruthenium and rhodium, but not over the other metals. Over iridium, particularly, it varied markedly, and the yield estimated by extrapolation to 0 % conversion was approximately 93 percent of propylene-d₂. This value was higher than observed on palladium. Thus, simple relationship available for all the metals between the yield of propylene-d₂ and that of propylene-cis-1,2-d₂ was not observed in the hydrogenation of methylacetylene, while in the hydrogenation of acetylene the yield of ethylene-cis-d₂ was found to be related to that of ethylene-d₂ by Bond et al.^{7), 8)} Over the respective metals however, the yield of cis-isomer increased with an increase of the yield of

propylene-d₂.

1) Pattern of deuterium distribution. Six metals can be classified roughly into two groups according to both distributions. (i) First group includes nickel, palladium and platinum, on which highly deuterium-substituted propylenes were not produced and methyl group of propylene was almost inert for deuterium substitution. Over palladium, particularly, there was a distinct cut-off in the fine distribution at propylene-d₃, and deuterium substitution for methyl group was not detected at all. In addition to the above results both distributions were constant during the first stage. This result requires such a condition that the composition of adsorbed species are constant during the reaction, especially, surface deuterium concentration which is expressed by the fraction of deuterium in the adsorbed hydrogens (H or D). Practically, very little deuterium returned from the surface to the gaseous phase in the form of HD or deuteromethylacetylene, and therefore the above condition would be established on the surface of the three catalysts. (ii) Second group of the metals includes rhodium, iridium and ruthenium, on which all possible deuteropropylenes were produced and methyl group was substituted by deuterium in an appreciable amount. Moreover, fine and hyperfine distributions of

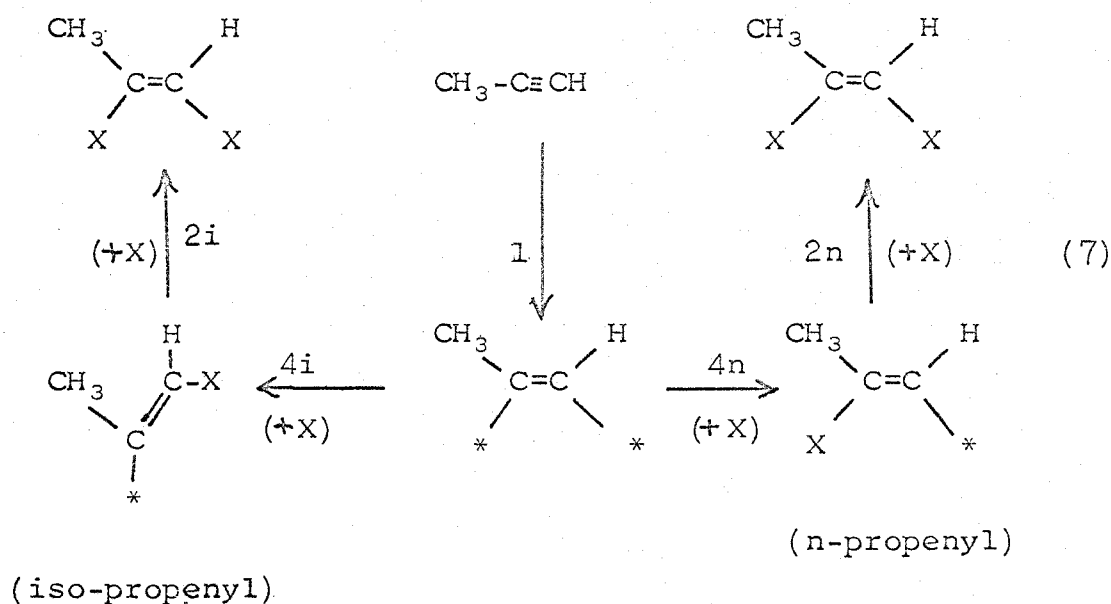
deuteropropylene varied as the reaction proceeded. This result would be caused by the variation of deuterium concentration on the surface. On these three metals, adsorbed deuterium atoms were returned to the gaseous phase as either HD or deuteromethylacetylene in a large amount, compared with the results on the first group metals. Such desorption processes would bring about lowering of the surface deuterium concentration and moreover variation of deuterium distribution.

2) Surface deuterium concentration. Each metal produced always propylene-d₀, -d₁ and -d₃ in addition to propylene-d₂, the most abundant product. This finding suggests that dissociative adsorption followed by scrambling of protium and deuterium takes place before addition to methylacetylene, and that consequently addition of hydrogen to carbon-carbon triple bond occurs atomically rather than molecularly. Further support of this conclusion is the fact that non-equilibrated protium and deuterium mixture gave a larger amount of propylene-d₁ than expected from the assumption that scrambling of protium and deuterium did not take place on the surface.

Recent infrared study²³⁾ of the adsorbed acetylene suggested that associative adsorption of acetylene ($\text{HC} \equiv \text{CH}$) is predominant over π -complex adsorption

$$\begin{array}{c} \text{HC} \equiv \text{CH} \\ | \quad | \\ * \quad * \end{array}$$

($\text{HC}\equiv\underset{\substack{| \\ *}}{\text{CH}}$) over alumina-supported platinum. Taking this result into consideration, the mechanism of methylacetylene hydrogenation is adequately represented by eq. (7).



Here, step numbers in this mechanism are the same as applied in eq. (4), and X denotes the surface hydrogen atom, H or D. For the hydrogenation of methylacetylene, two kinds of the half-hydrogenated states are obtainable, n-propenyl and iso-propenyl, so that step 4 is divided into two steps, 4_n and 4_i , according to the formation of n-propenyl and iso-propenyl, respectively. This mechanism explains easily the predominant formation of propylene- d_2 and also propylene-cis- d_2 . Propylene- d_0 and - d_1 are produced by the addition of adsorbed protium, which may be supplied to the surface by the

exchange reaction of methylacetylene with deuterium. Therefore, surface hydrogen, X in eq. (7), consists of deuterium and protium.

Surface deuterium concentration must be reflected in the mean number of deuterium atoms substituted at the methine position (2 position hereafter) of the produced propylene. The mean number of deuterium substituted at each position of propylene can be calculated by using the fine and hyperfine distributions, on the assumption that all the d_3 -, d_4 - and d_5 -isomers are composed mainly of $\text{CH}_3\text{-CD=CD}_2$, $\text{CH}_2\text{D-CD=CD}_2$ and $\text{CHD}_2\text{-CD=CD}_2$, respectively. This assumption may be reasonable, judging from the hyperfine distributions of propylene- d_1 and $-d_2$. Calculated values are summarized in

Table 14, together with the yield of propylene- d_1 and $-d_0$ which are made by addition of protium, for reference. In the table, cis-1 and trans-1 positions denote the methylene hydrogens with regard to the methyl group, while 2 and 3 positions denote the methine and methyl hydrogens, respectively. As shown in Table 14, mean number of deuterium at 2 position was the highest over palladium, and it decreased in the following order.



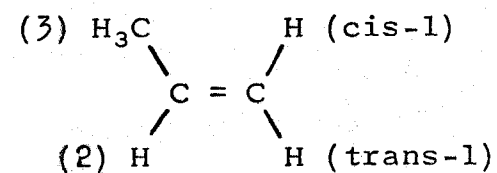
On the other hand, the yield of propylene- d_0 and $-d_1$

Table 14

Mean Number of Deuterium Atoms Substituted at Each
Position of Propylene at 70 % Conversion of the
Reaction, $\text{CH}_3\text{-C}\equiv\text{CH} + \text{D}_2$, at 25°

Catalyst	Position				Yield of propylene- d_0 and $-\text{d}_1$ (%)
	cis-1	trans-1	2	3	
Ni	0.54	0.73	0.80	0.01	20.6
Pd	0.19	0.84	0.92	—	12.5
Pt	0.26	0.79	0.90	0.00 ₅	14.4
Rh	0.53	0.73	0.74	0.10	22.7
Ir	0.39	0.83	0.83	0.15	17.8
Ru	0.59	0.82	0.81	0.16	14.5

$\text{P}^\circ_{\text{C}_3\text{H}_4} = 30 \text{ mm}, \quad \text{P}^\circ_{\text{D}_2} = 60 \text{ mm}$



decreased as the reverse of this order, except ruthenium. These findings suggest that mean deuterium number at 2 position reflects the surface deuterium concentration. Surface deuterium concentration is considered to be relatively high during the reaction and it may be more than 70 percent of the adsorbed hydrogens over all the metals.

Mean number of deuterium at 2 position was found to be related to that at cis-1 position, as shown in Fig. 11. This finding shows that methylacetylene has only one hydrogen atom, acetylenic hydrogen, of high exchangeability, and that methyl hydrogens are less exchangeable. Surface deuterium concentration may be lowered by the exchange of acetylenic hydrogen with deuterium. Similar conclusion can be derived from the fine distribution of deuteromethylacetylene produced by the hydrogenation over rhodium-black, where deuterated methylacetylene was returned to the gaseous phase in a large amount, as shown in Table 7f. The fine distribution of deuteromethylacetylene (No. 50) did not obey the random distribution, where three or four hydrogens are assumed to be equivalent for deuterium exchange. This discrepancy between calculated and observed distributions indicates that methylacetylene is not equivalent for deuterium exchange, and that almost all

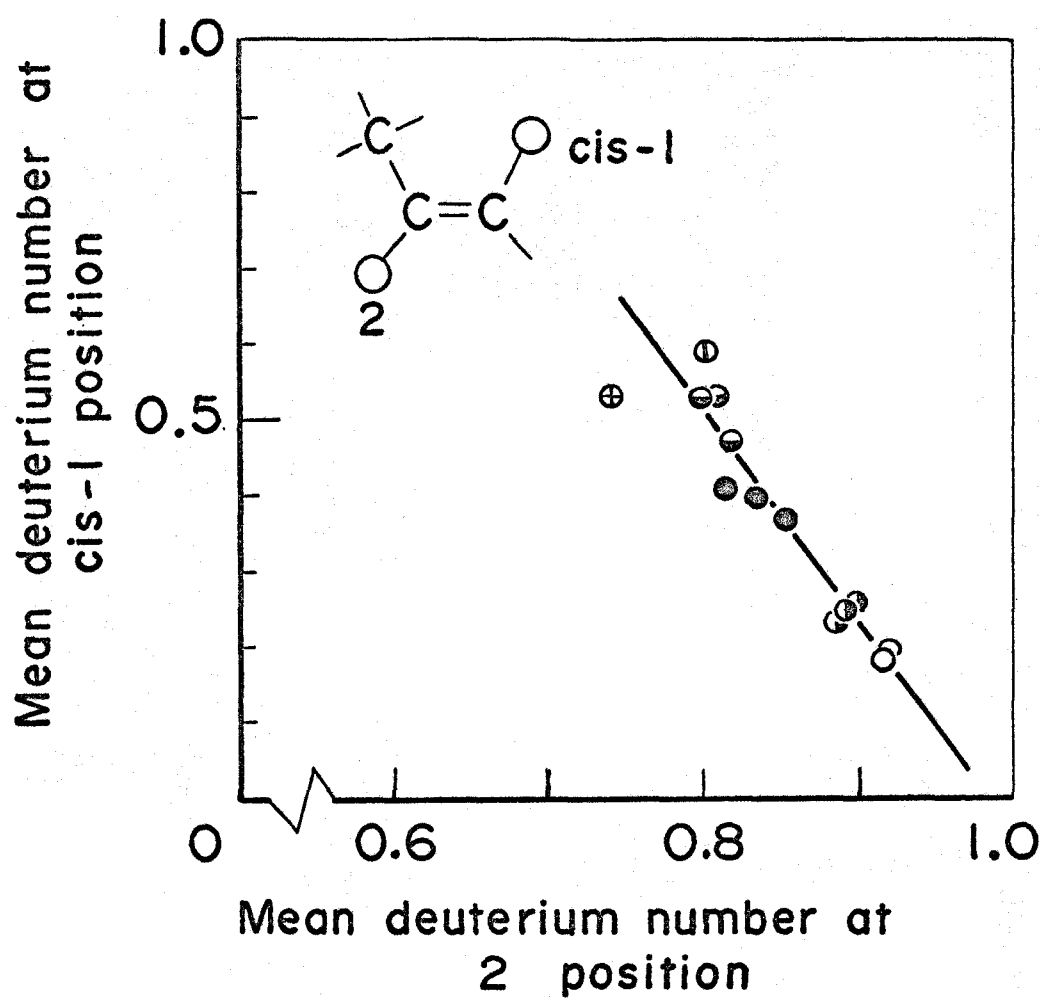
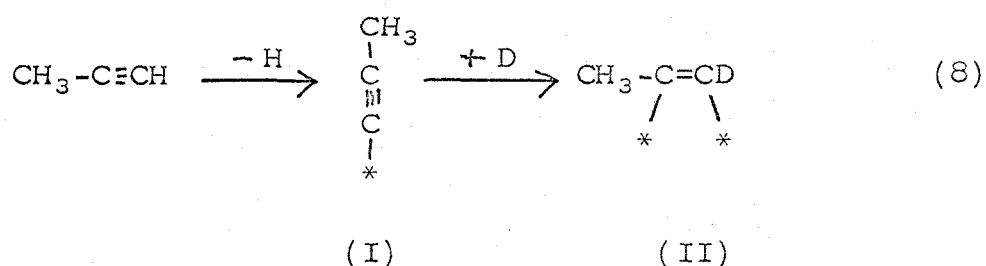


Fig. 11. Corelation between the mean deuterium number at cis-1 position and that at 2 position of propylene produced by the reaction of methyl-acetylene with deuterium at 25°.

the methylacetylene- d_1 may be $CH_3-C\equiv CD$. During the methylacetylene hydrogenation with deuterium, surface deuterium concentration was relatively high, while in the case of hydrogenation of propylene it was very low.^{16),24)} This remarkable contrast in the concentration can be explained by the difference of the number of exchangeable hydrogens, i.e., very exchangeable hydrogen of methylacetylene is only one, as mentioned above, whereas all the six hydrogens are exchangeable in propylene.

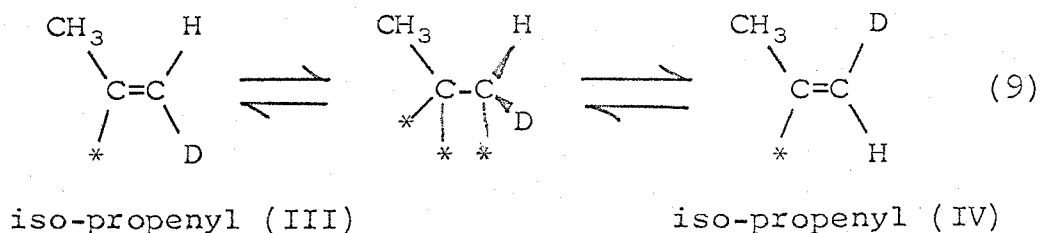
3) Formation of isotopic isomers. The observed formation of propylene-cis-1- d_1 , -trans-1,2- d_2 and -1,1- d_2 requires a mechanism for the exchange of the acetylenic hydrogen of methylacetylene. The first possible mechanism for the exchange is as follows.



In this mechanism, methylacetylene is assumed to be adsorbed by dissociating the acetylenic hydrogen and to pass into an associative adsorption (III) by addition of surface hydrogen without desorption from the surface. The above mentioned isomers are expected to be produced by the addition of surface hydrogens (H or D) to the

the first and second steps in the above scheme, so that such a large difference as observed will not be expected. Taking this finding into consideration, the mechanism in eq. (8) may be of minor importance for the exchange of acetylenic hydrogen of methylacetylene.

On the other hand, the linear relationship between the yield of propylene-trans-1,2-d₂ and that of propylene-cis-1,2-d₂, shown in Fig. 12, may give the final scheme; i.e., two groups of metals, as stated in a previous section (IV-3-1), give two separate straight lines whose slopes are approximately the same. These straightlines indicate that the trans isomer may be produced at the expense of the cis isomer. However, the trans isomer is not produced by the subsequent isomerization of the gaseous cis-isomer which is produced predominantly by the mechanism (7) in the first stage, as stated in a previous section (IV-1). This means that isomerization equilibrium between cis and trans isomers must exist before the desorption of propylene. Such a situation is fulfilled by the following equilibrium between two isotopic isomers of iso-propenyl (III) and (IV).



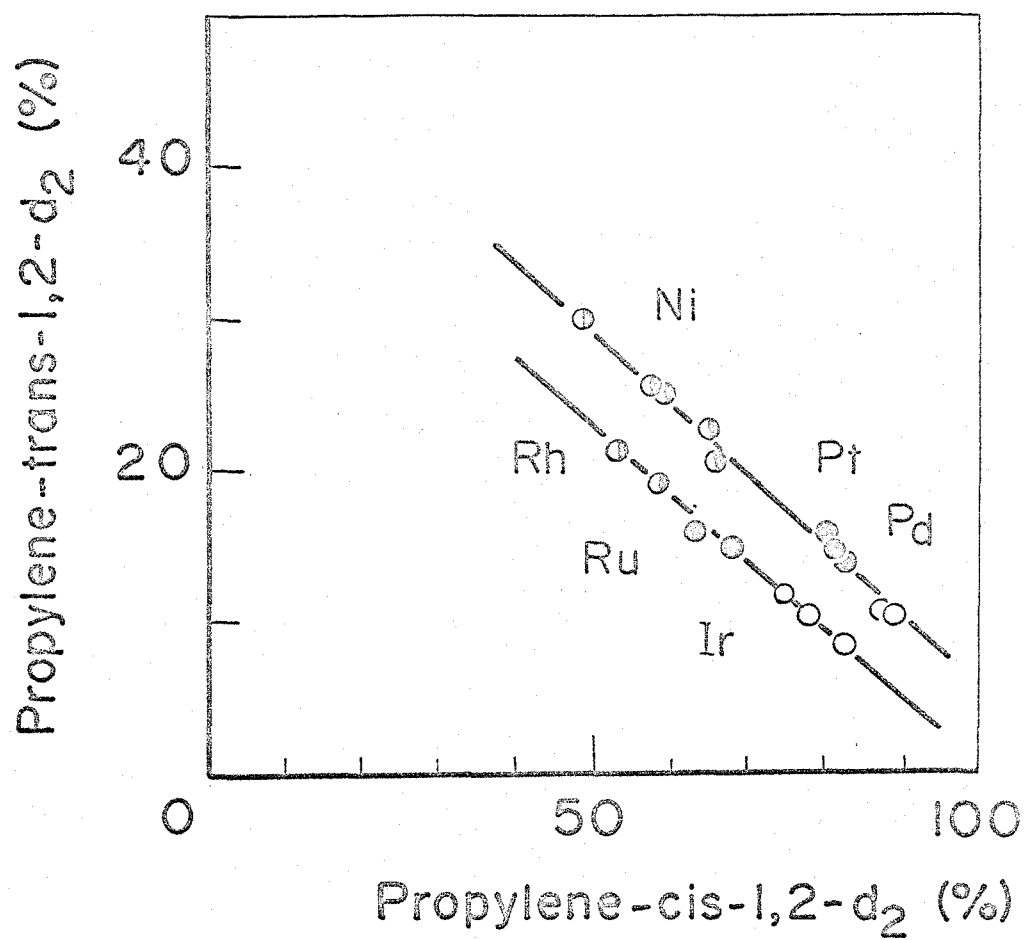
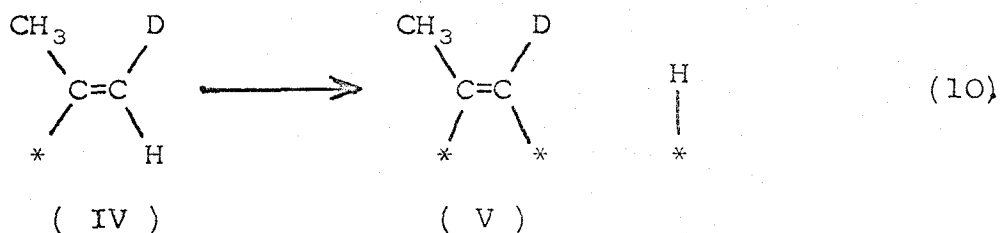


Fig. 12. Corelation between the yield of propylene-trans-1,2-d₂ and that of propylene-cis-1,2-d₂ produced by the reaction of methylacetylene with deuterium at 25°.

Similar equilibrium may also exist in the case of n-propenyl. Bond et al.^{7),8)} proposed similar mechanism for the isomerization between cis and trans isomers of di-deuteroethylene during the hydrogenation of acetylene with deuterium, but they adopted a free radical ($\overset{\circ}{\text{DC}}\text{-CHD}$) as an intermediate.

The equilibration mechanism (9) can easily explain the formation of several isotopic isomers of propylene- d_1 and $-\text{d}_2$ (cis-1- d_1 , trans-1- d_1 , 2- d_1 , cis-1,2- d_2 and trans-1,2- d_2) by the addition of a protium atom or a deuterium atom to (III) and (IV). The reverse reaction of (IV) to the associatively adsorbed methylacetylene release a protium atom on the surface and forms adsorbed deuteromethylacetylene (V). Addition of one protium atom



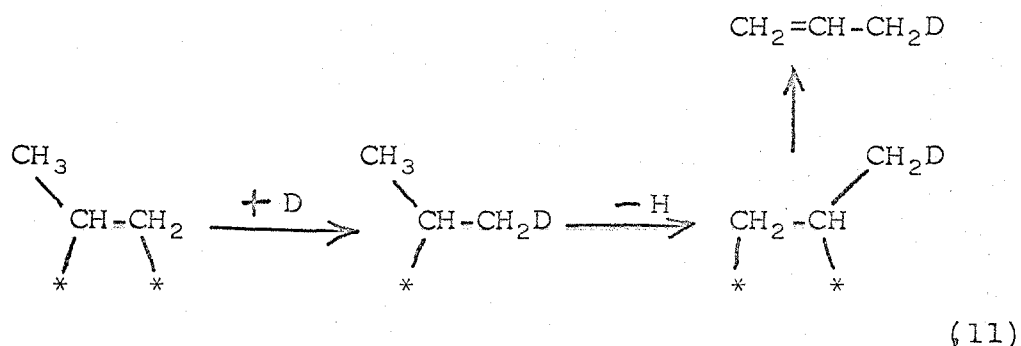
and one deuterium atom to (V) forms propylene-trans-1,2- d_2 or 1,1- d_2 . Propylene- d_3 is also produced by the addition of two deuterium atoms to (V).

The surface deuterium concentration is lowered by the protium atom released from methylacetylene via eq. (10), so that it may be related to the degree of the exchange reaction of methylacetylene by the mechanism

(9) and (10). The surface deuterium concentration is estimated to lie in the ranges 70-90 % of the total surface hydrogen, judging from the mean number of deuterium atoms substituted at 2-position of the produced propylene in Table 14. This finding indicates that the exchange reaction of methylacetylene with deuterium occurs in fairly large extent. However, amount of the produced deuteromethylacetylene was very small over all the metals, except rhodium where a large amount of methylacetylene -d₁ was produced. Taking these findings into consideration, methylacetylene-d₁, CH₃-C≡CD, seems to exist on the surface in comparatively large concentration, but owing to the slow rate of its desorption over all the metals except rhodium, its amount in the gaseous phase may be very small.

4) Double-bond migration. Methyl group was almost or completely inert for deuterium substitution over the first group of metals (palladium, platinum and nickel), while it was substituted by deuterium in an appreciable amount over the second group of metals (rhodium, iridium and ruthenium). The latter group of metals, except rhodium, exhibited very low selectivities for propylene formation. Over these metals, it is expected that adsorbed propylene, which is produced by the hydrogenation of methylacetylene and remains undesorbed, may exist in

a large amount. Therefore, following propylene-propyl interconversion shown by eq. (11) is considered to occur in a large extent over iridium and ruthenium.



This interconversion accompanies double bond migration, so that even the methyl group is substituted by deuterium.

From this point of view, it is concluded that deuterium substitution for the methyl group over the second group metals takes place through the process where propylene is produced from methylacetylene.

This scheme is the same as observed in the case of propylene hydrogenation with deuterium,²⁶⁾ because methyl deuterated propylene was produced via eq. (11).

However, such a result could not be obtained over the first group of metals probably due to the poisoning effect of methylacetylene to the process.

SUMMARY

By applying the microwave spectroscopy to the catalytic hydrogenation of methylacetylene with deuterium over Group VIII metals (Ni, Pd, Pt, Rh, Ir and Ru), the distributions of isotopic isomers of mono- and di-deuteropropylenes produced by the reaction were successfully determined. From the distributions the following conclusions with regard to the mechanism of its hydrogenation were derived.

i) Propylene-trans-1,2-d₂ and 1,1-d₂ are produced at the expense of propylene-cis-1,2-d₂ through the path where propylene is formed from methylacetylene on the surface.

ii) Methyl deuterated propylenes are produced by propylene-propyl interconversion which accompanies double-bond migration.

iii) Surface deuterium concentration is higher than in the reaction of propylene with deuterium, and the concentration is reflected in the mean number of deuterium atoms at the methine position of the produced propylene.

These conclusions were used in discussing the mechanism of methylacetylene hydrogenation, and some of the adsorbed states of the reactant could be concluded.

Moreover, by using the distributions, six metals were classified roughly into two groups in the catalytic behavior of deuteration. The first group included Ni, Pd and Pt, while the second group Rh, Ir and Ru. Over the first group, the double-bond migration was almost or completely prohibited by the strong adsorption of methylacetylene, but over the second group not significantly. These points are worthy of mention, because such examples may be difficult without use of the microwave spectroscopy.

Selectivity for propylene formation in the hydrogenation was also investigated by gas chromatography. Palladium-black was the most selective of the six metals for the reaction, and the order of the selectivity was as follows.



This order is concordant with the order of selectivity for ethylene formation in the hydrogenation of acetylene over evaporated metal films.

Allene, an isomer of methylacetylene, was produced during the hydrogenation of methylacetylene over ruthenium-black, but its formation was concluded to be independent of the hydrogenation.

The isomerization between methylacetylene and allene over ruthenium-black was studied kinetically, so that

the following interesting findings were obtained.

i) Ruthenium-black was found to exhibit a high activity for the isomerization, while other metals were much less active and their activities were $10^{-2} \sim 10^{-3}$ of that of ruthenium-black.

ii) The equilibrium concentrations of both species were found to be very different from the theoretical values.

Moreover, the mechanism of the isomerization was estimated mainly by the study of the deuterium distributions in the deuteromethylacetylenes and deuterio-allenes.

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