On the Selectivity in the Catalytic Hydrogenation of Methylacetylene on Group VIII Metals

Noritetsu YOSHIDA* and Kozo HIROTA**

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

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The reaction of methylacetylene with hydrogen and deuterium was studied over five Group VIII metals (Pd, Pt, Rh, Ir, and Ru) at 25 °C. Among these metals, palladium was the most selective for the propylene formation; the selectivity varied from metal to metal (Pd>Pt>Rh>(Ni)>Ru>Ir). A new result was obtained over ruthenium; the isomerization of methylacetylene to allene occurred simultaneously with the hydrogenation over only this metal. In the reaction with deuterium, the stereoselectivity of the metals was investigated on the products by analyzing them by the microwave spectroscopic and mass spectrometric methods. Only three hydrogen atoms were deuterated in the propylene produced over Ni, Pd, and Pt; in conformity with the above, the deuterated positions of propylene-d_1 and -d_2 were limited to three in the methylene and methylidyne groups. No such tendency was observed for Ir, Rh, and Ru, where the methyl hydrogens were also deuterated. The relative yield of the *cis*-1,2-d_2 species, always the most abundant product, decreased in this order: Pd>Pt>Ir>Ru>(Ni)>Rh at 70% conversion. A reaction mechanism which explains the relative yields of isotopic isomers of deuteropropylenes except for the methyl-deuterated species was proposed, assuming an adsorbed radical as an intermediate. The calculated isomer distributions based on the scheme coincided well with those observed in the cases of Pd, Pt, and Ni, but not in those of Ir, Rh, and Ru.

For the catalytic hydrogenation of acetylenic compounds, there have been many investigations of the kinetics, but few about reactions with deuterium. Detailed results on the reaction of dimethylacetylene with deuterium were reported by Meyer and Burwell1) using palladium–alumina, and by Webb *et al.*2) using other noble Group VIII metals supported on alumina. Recently, Bond *et al.*3,4) studied the reaction of acetylene with deuterium using noble Group VIII metals supported on alumina, and determined the relative yields of the isomeric ethylene-d_2 species by infrared spectroscopy.

From these studies, it is now definitely accepted5) that the major process involved in producing an olefin from its corresponding acetylenic compound over metal catalysts is the successive addition of two hydrogen atoms, not the direct addition of a hydrogen molecule, as has usually been presumed before. However, the previously-proposed scheme cannot explain the observed results quantitatively; for instance, *trans*-olefin is always produced to some extent as the primary product, though in a much smaller quantity than *cis*-olefin.

In order to clarify this point, in the present research the stereoselectivity in the reaction of methylacetylene with deuterium was investigated over five Group VIII metals (Pd, Pt, Rh, Ir, and Ru) by measuring with a microwave spectrometer the relative yields of the isotopic isomers of the propylene-d_1 and -d_2 produced. The mechanism of stereoselectivity is discussed on the basis of the results for the five metals and those for Ni previously reported.6)

Experimental

Materials. The purifications of methylacetylene, deuterium (Takachiho Chem. Ind. Co.) and electrolytic hydrogen were described in a previous report.6) The rhodium-black was prepared by the reduction of the rhodium hydroxide produced by the reaction of rhodium trichloride with sodium hydroxide. The iridium-black was prepared by adding a 0.01 mol solution of iridium tetrachloride to an excess amount of a hot solution of sodium borotetrahydride. The palladium-black, platinum-black (Nakarai Chem. Co.) and ruhtenium-black (Mitsuwa Chem. Co.) used were commercial reagents. All the metals mentioned above were, before use, reduced with hydrogen at 230—240 °C for two days in the reaction vessel. The amount of each metal used and the BET areas (mesured with N_2 at −198 °C) are as follows:

Pd	2 mg (7.7 m^2/g),	Pt	40 mg (2.4 m^2/g),
Rh	30 mg (10.9 m^2/g),	Ir	20 mg (14.2 m^2/g),
Ru	150 mg (33.2 m^2/g).		

Procedure. The reaction of methylacetylene with hydrogen or deuterium was carried out under the same conditions and by the same procedure over all the five metals, as has previously been done over nickel.6)

The standard mixture, which consisted of P_{D_2} (or P_{H_2})= 60 mmHg and $P_{C_3H_4}$=30 mmHg, was introduced into a reaction vessel (about 300 ml) containing the catalysts; this vessel was connected to a conventional vacuum apparatus. The reactions were carried out in a simple static system at 25 °C and followed from manometric measurements. When the desired degree of hydrogenation has been reached, the reaction mixture was taken out by expanding it into a reservoir (3 l) preliminarily evacuated. The composition of hydrocarbons in the mixture was analyzed by gas chromatography, using a 4 m column of 20 wt% of dimethylsulfolane on Neopak-1B at room temperature. The samples for the isotopic analysis were prepared by the gas-chromatographic separation of the mixture into components (propane, propylene, and methylacetylene) using the column described above.

The deuterium distributions in the propylene and methylacetylene produced were determined with a mass spectrometer (Hitachi RMU-5B) in the Institute for Protein Research,

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* Sagami Chemical Research Center, Nishi-Ohnuma, Sagamihara Kanagawa 229, (Present address, 3–59–1–510 Yamatedai, Ohkubo, Akashi, Hyogo 674.)

** Present address, Chiba Institute of Technology, Yatsu, Narashino, Chiba 275.

Osaka University. In the analysis, the energy of the ionizing electrons was lowered sufficiently so that only the parent ion could be produced in the mass spectrum.

Propylene-d_1 (C_3H_5D) and -d_2 ($C_3H_4D_2$) have four and seven species of isotopic isomers respectively, as is shown in Fig. 1. The relative abundances of these species in the propylene produced were determined with a microwave spectrometer, installed at the Sagami Chemical Research Center, by measuring the relative intensities of the rotational 1_{01}—0_{00} transitions of the species. A detailed description of the analysis has previously been reported.[7] The distributions of the isotopic isomers thus determined are called the hyperfine distributions of propylene-d_1 and -d_2 respectively in order to discriminate them from the usual deuterium distribution, called the fine distribution, which is determined with a mass spectrometer.

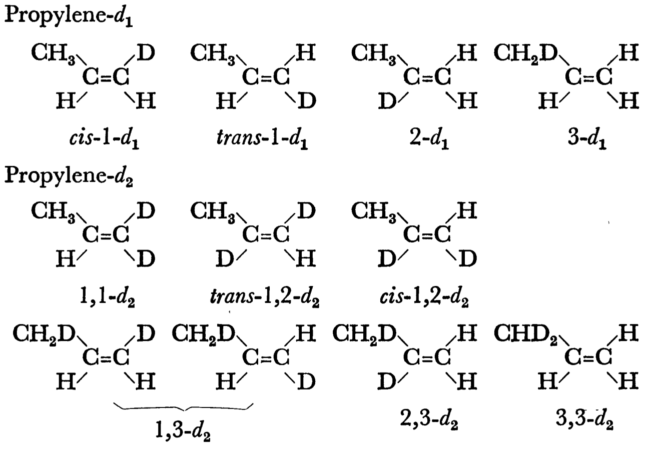


Fig. 1. Isotopic isomers of propylene-d_1 and -d_2

Results

Reaction Curves. Some typical reaction curves with the standard mixture of hydrogen (or deuterium) and methylacetylene over six metals are shown against the time in Fig. 2, taking the pressure fall ($-\Delta P$) as the ordinate. As is shown in this figure, all the curves consist of two parts with different rates, producing a point called the acceleration point ($-\Delta P_a$). The reaction rates are accelerated abruptly at this point, except in the case of palladium, where negative acceleration is observed. Each part can be regarded as corresponding to a reaction stage, as has been confirmed by another finding. The possibility of polymerization during the reaction may be ruled out over the six metals, because the total pressure decreases asymptotically to the value expected from the stoichiometric equation; $C_3H_4+2H_2=C_3H_8$. This situation is supported by the fact that no polymers were detected in the gas phase.

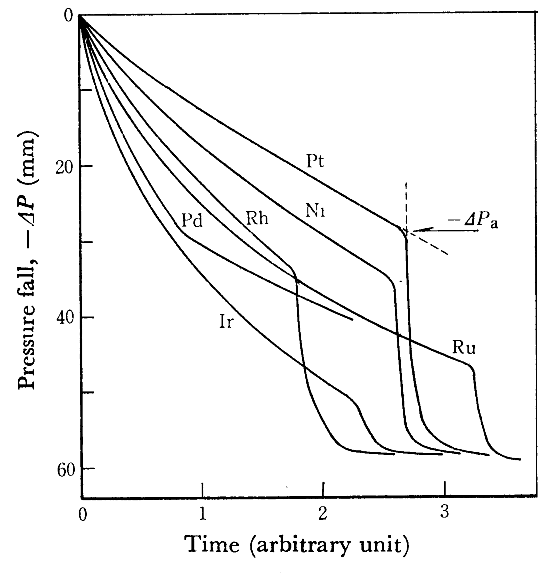


Fig. 2. Typical pressure-fall against time curves for the hydrogenation of 30 mm of methylacetylene at 25 °C. Ni, Pt, Ir $P^\circ_{H_2}=60$ mmHg; Pd, Rh, Ru $P^\circ_{D_2}=60$ mmHg.

The rates of the pressure fall during the course of the former stage was approximately proportional to the remaining hydrogen pressure. Furthermore, the initially-added propylene (26 mm) did not affect the hydrogenation rate over Ir, in accord with the results for 2-butyne with 1-pentene added[8] and that of acetylene with ethylene added.[9,10] The catalytic activities of the six metals were compared with one another by calculating the initial rate of methylacetylene removal per unit of area. The results in the reaction with deuterium were as follows:

A: Pd > Rh > Pt > Ni > Ir > Ru

A similar sequence has previously been reported in the hydrogenation of acetylene over evaporated metal films,[11] *i.e.*, Pd>Rh>Pt>Ni≫Fe>W. However, the A sequence does not coincide very well with that over supported metals.[12]

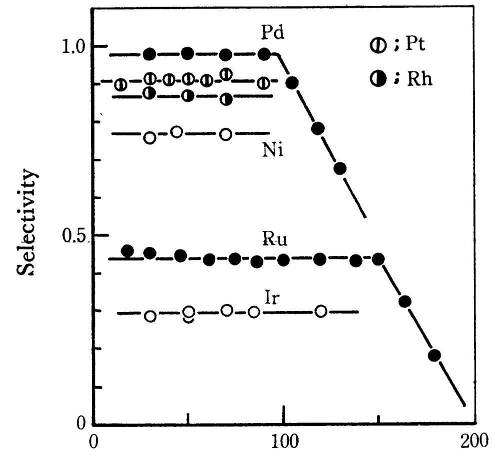


Fig. 3. Selectivity against conversion curves for the hydrogenation of methylacetylene at 25 °C. $P^\circ_{C_3H_4}=30$ mmHg, $P^\circ_{D_2}=60$ mmHg.

Selectivity. The selectivity, defined by $S=P_{C_3H_6}/(P_{C_3H_6}+P_{C_3H_8})$, was determined at various conversions of the reaction between methylacetylene and deuterium. It is shown in Fig. 3 against conversion which is defined by the percentage of the total pressure fall to the initial pressure of methylacetylene. The mean values of the selectivity, which is very different from metal to metal, are the following sequence:

B: Pd(0.98) > Pt(0.92) > Rh(0.87) > Ni(0.76) > Ru(0.44) > Ir(0.29).

This sequence is the same as that reported in the case of acetylene.[13)]

The selectivity in the former stage is constant within the limits of experimental error, but it decreases rapidly in the latter stage, as is shown by the right halves of the corresponding curves of Pd and Ru in the figure. This finding indicates that methylacetylene is hydrogenated in the former stage to both propylene and propane in a certain ratio, while further hydrogenation of propylene to propane becomes dominant in the latter stage.

Formation of Allene. In the course of hydrogenation over ruthenium, a new finding was obtained; a trace of allene ($CH_2=C=CH_2$), which is an isomer of methylacetylene, appeared in the reaction mixture, together with the hydrogenation products. At a 70% conversion, the allene amounted to 4.3% of the initial methylacetylene. Allene was formed also in the absence of hydrogen over ruthenium; the initial rate of its formation was 1.8×10^{-6} mol/m^2·hr. This value was close to the rate of the hydrogenation, 6.8×10^{-5} mol/m^2·hr, represented by the rate of methylacetylene removal in the gas phase; therefore, allene could be detected during the hydrogenation. Over the other metals, however, allene could not be detected at all either during the hydrogenation or in the absence of hydrogen at 25 °C.

The high activity of ruthenium for the isomerization ($CH_3-C\equiv CH \rightleftarrows CH_2=C=CH_2$) might be accounted for by its crystal structure, because ruthenium has the closed-packed hexagonal structure, whereas the other metals have the face-centered cubic structures. Further experiments will be required to confirm this supposition. The detailed results of the isomerization will be reported in the next paper.

Deuterium Distribution. The fine and hyperfine distributions of the propylene produced over palladium are shown in Table 1, where $\phi/100$ denotes the mean number of deuterium atoms in a propylene molecule; *i.e.*, $\sum i.d_i/100$ ($i=1$, 2, ---, 6). The measurement errors in the hyperfine distributions are indicated by 2.5 σ (σ: the standard deviation). Table 1 shows that neither the fine nor the hyperfine distribution changes substantially until the acceleration point or 97% conversion of the hydrogenation. Such constancy of the distribution was also observed in the case of nickel, as has previously been reported.[6)] After the acceleration point, however, both distributions of propylene become dispersed, producing various kinds of species.

The fine and hyperfine distributions over six metal catalysts at a 70% conversion are compared in Tables 2 and 3 respectively. In Table 2, the fine distribution of methylacetylene is also listed. Table 2 shows that the most abundant deuteropropylene is the d_2 species,

TABLE 1. PALLADIUM-CATALYZED REACTION

Fine distributions (%)

No.	Conv. (%)	Propylene							$\phi/100$
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	
16	50	$1._1$	$11._1$	$79._2$	$8._6$	—	—	—	1.95
15	70	$0._9$	$11._6$	$78._5$	$9._0$	—	—	—	1.96
44	90	$0._8$	$9._1$	$79._2$	$10._9$	—	—	—	2.00
43	105	$0._7$	$9._1$	$72._9$	$15._3$	$0._9$	$0._6$	$0._5$	2.10
42	118	$0._8$	$9._0$	$63._9$	$21._7$	$2._2$	$1._4$	$1._1$	2.24
41	130	$0._9$	$8._3$	$50._1$	$29._2$	$5._4$	$3._6$	$2._6$	2.51

Hyperfine distributions (%)

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

$P^0_{C_3H_4}=30$ mmHg, $P^0_{D_2}=60$ mmHg, a) 3-d_1, 1,3-d_2, and 3,3-d_2 species were not detected, b) 30% conversion.

TABLE 2. FINE DISTRIBUTIONS (%) OF METHYLACETYLENE AND PROPYLENE AT 70% CONVERSION

	Methylacetylene			Propylene							$\phi/100$
	d_0	d_1	d_2	d_0	d_1	d_2	d_3	d_4	d_5	d_6	
Pd	($98._1$	$1._9$	—)*	$0._9$	$11._6$	$78._5$	$9._0$	—	—	—	1.96
Pt	$96._8$	$3._2$	—	$1._0$	$13._4$	$75._2$	$9._8$	$0._5$	—	—	1.95
Rh	$57._3$	$42._4$	$0._3$	$3._1$	$19._6$	$47._7$	$25._7$	$2._1$	$1._1$	$0._7$	2.10
Ir	$98._3$	$1._7$	—	$1._3$	$16._0$	$55._0$	$20._4$	$2._8$	$2._4$	$1._6$	2.20
Ru	($85._1$	$14._9$	—)*	$1._7$	$12._8$	$45._4$	$32._8$	$3._2$	$2._2$	$1._9$	2.37
Ni	$98._6$	$1._4$	—	$1._8$	$18._8$	$49._6$	$29._1$	$0._7$	—	—	2.08

$P^0_{C_3H_4}=30$ mmHg, $P^0_{D_2}=60$ mmHg *( ); Distribution at 50% conversion.

TABLE 3. HYPERFINE DISTRIBUTIONS OF PROPYLENE-d_1 AND -d_2 AT 70% CONVERSION

	Propylene-d_1 (%)				Propylene-d_2 (%)					
	c-1-d_1	t-1-d_1	2-d_1	3-d_1	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
Pd	5.7±0.5	49.8±7.8	44.6±8.2	—	1.0±0.1	11.3±0.5	87.7±0.5	—	—	—
Pt	8.6±0.5	43.3±5.6	48.1±6.2	—	2.8±0.2	16.0±0.8	81.2±0.6	—	—	—
Rh	17.4±0.5	37.0±2.0	42.8±2.7	2.8±0.5	20.8±1.2	21.2±3.0	53.3±1.8	1.4±0.3	1.5±0.2	1.8±0.3
Ir	9.4±0.3	45.8±2.0	43.7±3.8	1.1±0.3	9.1±0.6	10.4±0.4	78.0±0.9	0.6±0.2	1.0±0.2	0.9±0.1
Ru	16.2±0.9	42.8±6.0	37.7±3.6	3.3±0.6	19.8±1.3	17.4±1.6	58.2±1.7	1.3±0.6	2.7±0.5	0.6±0.1
Ni	16.7±0.9	37.1±3.0	45.3±6.7	0.9±0.3	15.9±2.4	25.5±1.9	57.7±1.9	—	0.9±0.2	—

$P^0_{C_3H_4}=30$ mmHg, $P^0_{D_2}=60$ mmHg, 25 °C.

but it is not the unique product, over every metal. Propylenes more highly deuterated than d_4 are not produced over Pd; similarly, their amounts are not significant over Pt and Ni. This finding is in accord with the results shown in Table 3; *i.e.*, the deuterium atom is not substituted for the hydrogen atoms in the methyl group of a propylene molecule. The constancy of the distributions until the acceleration point was observed over Pt as well as over Pd and Ni. Over the other metals, however, the yield of the propylene-d_2 species decreased slightly as the reaction proceeded. Simultaneously, the relative yield of the *cis*-1,2-d_2 species decreased; for example, the yields over Rh and Ru at a 30% conversion were 58.6 and 63.4% respectively, while that over Ir at a 50% conversion was 82.7%.[14]

It is interesting that methylacetylene-d_1 was formed markedly in the cases of Rh and Ru. According to the microwave spectroscopic analysis of methylacetylene at a 50% conversion over Rh, methylacetylene-d_1 consisted of 99.8% $CH_3\text{–}C{\equiv}CD$ and 0.2% $CH_2D\text{–}C{\equiv}CH$. The methylacetylene-d_1 produced over the other metals is estimated to be almost $CH_3\text{–}C{\equiv}CD$, just as over Rh, because methylacetylenes more highly deuterated than d_2 could not be detected practically, as is shown in Table 2.

The dependence of the fine and hyperfine distributions on the experimental conditions was studied over Ni, following the previous report.[6] The results are shown in Table 4. When the initial partial pressure of deuterium was increased from 60 to 150 mm, neither of the distributions changes very much. An increase in the temperature, however, reduces the yield of *cis*-1,2-d_2 species slightly. The former result is in accordance with the constancy of the distributions until the acceleration point, as described above; a very similar tendency is estimated in the hyperfine distributions over Pd and Pt as well as over Ni.

Discussion

General. The finding that the selectivity remained constant up to the acceleration point can be explained by the stronger adsorption of methylacetylene than that of propylene or propane. This is supported by the fact that the initial rate was not affected by the initially-added propylene over Ir. Therefore, methylacetylene is considered to act as poison in the hydrogenation of propylene. However, it is noteworthy that differences in selectivity are found among the metals. This may be ascribed to the degree of the adsorbability of methylacetylene to each metal, which determines the ratio of the probability of producing propylene (Path A) to that of producing propane *via* the half-hydrogenated species (Path B).

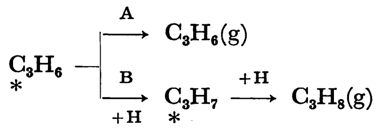


TABLE 4. NICKEL-CATALYZED REACTION

Fine distributions (%) at 70% conversion

No.	P^0_{MA} (mm)	$P^0_{D_2}$ (mm)	Temp. (°C)	MA		Propylene							$\phi/100$
				d_0	d_1	d_0	d_1	d_2	d_3	d_4	d_5	d_6	
5	30	60	25	$98._4$	$1._6$	$2._0$	$18._4$	$49._6$	$29._7$	$0._3$	—	—	2.08
7	30	150	25	$98._8$	$1._2$	$1._8$	$17._5$	$53._9$	$26._7$	$0._1$	—	—	2.06
13	30	60	0	$99._6$	$0._4$	$1._8$	$18._6$	$52._6$	$26._7$	$0._3$	—	—	2.05
14	30	60	50	$98._2$	$1._8$	$2._3$	$16._4$	$46._8$	$32._6$	$0._9$	$0._5$	$0._5$	2.17

Hyperfine distributions (%) at 70% conversion

No.	Propylene-d_1				Propylene-d_2[a)]			
	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
7	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	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	19.7±0.9	32.9±4.5	46.6±3.0	0.8±0.2	48.9±1.0	29.8±2.6	21.3±0.6	<0.2

a) 1,3-d_2 and 3,3-d_2 were not detected.

After the acceleration point in the reaction curve, the metallic surface is practically covered with olefin as a result of the rapid decrease in methylacetylene, so the selectivity in the former stage decreases gradually. As can be understood easily by the material balance, the higher the selectivity in the former stage, the later the acceleration point has to be for each metal.

The poisoning effect of strongly-adsorbed methylacetylene can also explain the findings that the fine and hyperfine distributions remained constant up to the acceleration point over Pd, Pt, and Ni. In the first stage of the reaction, deuterium exchange through the readsorption of the produced propylene cannot proceed because of this effect. After the acceleration point, however, propylene can readsorb with less of the poisoning effect of the methylacetylene than before that point. Consequently, the redistribution of hydrogen atoms among propylenes can proceed easily before propane is formed, various kinds of isomeric species being thus formed. This tendency is the same as that observed in the case of 2-butyne hydrogenation over palladium supported on alumina;[8] *i.e.*, *cis*-2-butene, the main product of the reaction, began to isomerize to *trans*-2- and 1-butene after the 2-butyne has almost disappeared from the gas phase. The small variation in the deuterium distributions with the time over Rh, Ir, and Ru cannot be explained only by this effect. An explanation of the finding requires the contribution of some surface processes which are of no importance in the cases of Pd, Pt, and Ni—for example, the processes leading to the formation of highly-deuterated propylenes, as will be discussed below.

Stereoselectivity. Table 3 shows that propylene-*cis*-1,2-d_2 is always the most abundant, indicating the *cis*-type addition of two hydrogen atoms to the triple bond to be very easy. Though this tendency has already been reported for several acetylenic compounds,[5] it must be noted that the reason for the favorable production of the *cis*-1,2-d_2 species over the *trans* isomer is due not to the thermodynamic but to the kinetic nature, because the two species are different only in the substituted position of deuterium, so their stabilities must be nearly the same.

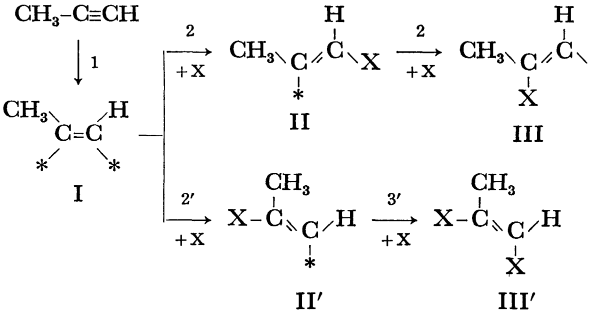
The relative yield of the *cis*-1,2-d_2 species over the six metals at 70% conversion decreased in this order;

$$\text{C:}\quad \text{Pd} > \text{Pt} > \text{Ir} > \text{Ru} > (\text{Ni}) > \text{Rh}.$$

Palladium is also superior in stereoselectivity to produce the *cis*-1,2-d_2 species. The C sequence is practically the same as the sequence of the selectivity for producing propylene-d_2 formation—*i.e.*, Pd>Pt>Ir>Ni>Rh>Ru, as is shown in Table 2. The different positions of Ru in the two sequences might be related to the formation of allene during the reaction, which occurred only over ruthenium.

The especially high stereoselectivity of palladium has already been established. According to Burwell's research into the hydrogenation of gaseous dimethylacetylene (2-butyne),[8] *cis*-2-butene was produced exclusively over alumina-supported palladium as long as any unreacted dimethylacetylene remained. Such a surprisingly high stereoselectivity was not observed, however, in the case of methylacetylene in the present research. In the hydrogenation of acetylene with deuterium by Bond and Wells, the high stereoselectivity could not be obtained, either.[3] In this study, they determined the relative yields of three kinds of isomeric ethylene-d_2, such as *cis*-d_2, *trans*-d_2, and *asymmetric*-d_2, by means of infrared spectrometry; they reported that the yield of the *cis*-d_2 species was about 80% over Pd. These results may be due to the steric hindrance of methyl groups bonded to the C≡C group rather than to such an experimental difference as that a flow method was adopted in the case of dimethylacetylene. The above findings may be useful in discussing the mechanism of the hydrogenation process of methylacetylene, $CH_3\text{-}C{\equiv}CH + H_2 \longrightarrow CH_3\text{-}CH{=}CH_2$.

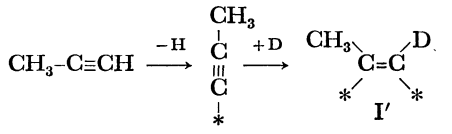
Mechanism. From the finding that the majority of the produced propylene consisted of the *cis*-1,2-d_2 species, Scheme (3) may be drawn for the mechanism of methylacetylene hydrogenation. It is based on the "associative mechanism," which is similar to that proposed for the catalytic hydrogenation of olefins.



(3)

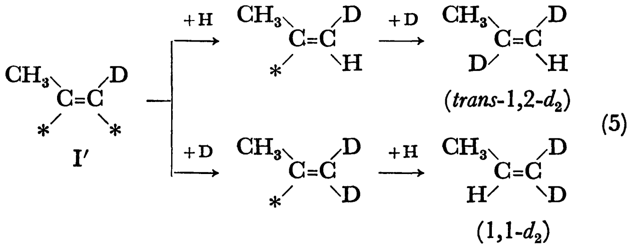
In this scheme, X denotes the adsorbed H or D atom, and the adsorbed species, I, is supported by the IR spectroscopic studies of adsorbed acetylene over silica-supported palladium[15] and alumina-supported platinum.[16] Propylene-*trans*-1-d_1 and 2-d_1 can also be produced through these processes by the addition of one protium and one deuterium atom to I species, but the propylene-*trans*-1,2-d_2, 1,1-d_2 and *cis*-1-d_1 species can not be produced thus. For the formation of the latter three isomers, some possible processes in addition to Scheme (3) might be added; they will be discussed below.

Firstly, the process concerned with producing associatively-adsorbed deuteromethylacetylene ($CH_3\text{-}C{\equiv}CD$, I′), as is shown by Process (4), is possible:



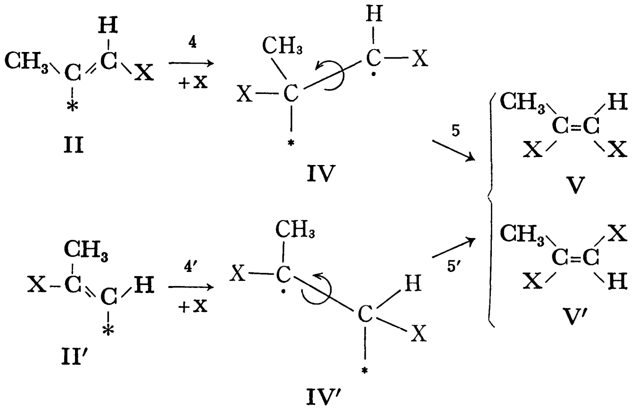
$$CH_3\text{-}C{\equiv}CH \xrightarrow{-H} \overset{CH_3}{\underset{*}{C{\equiv}C}} \xrightarrow{+D} \underset{\text{I}'}{(CH_3)(*)C{=}C(D)(*)} \qquad (4)$$

Methylacetylene is assumed in this process to be adsorbed by dissociating the acetylenic hydrogen and to pass into an associative adsorption by the addition of surface hydrogen without desorption from the surface. This process corresponds to that already proposed in the case of 1-butyne.[1] The extended scheme, (3) and (4), can explain the formation not only of propylene-*trans*-1,2-d_2, 1,1-d_2 and *cis*-1-d_1, but also of propylene-d_3, depending on whether I′ is attacked by H or D. However, the extended scheme is not yet sufficient to explain their yields quantitatively, since the *trans*-1,2-d_2 and 1,1-d_2 species can be expected to be produced in equal amounts from I′, as is shown by Process (5), contrary to the experimental results obtained over Pd, Ni, and Pt.



Over Pd particularly, the observed yield of propylene-*trans*-1,2-d_2 was ten or more times that of propylene-1,1-d_2. Now, even if the isotope effect is considered, it will be nearly compensated for by the first and second steps in Process (5), so that the large difference observed can not be expected on the basis of the extended scheme, (3) and (4), alone. Therefore, the contribution of another process, which will be discussed in the next paragraph, must be considered in addition to the contribution of Processes (3) and (4).

Secondly, the processes including an adsorbed propyl radical might be added to Scheme (3) as competitive, as is shown in Process (6). The IV and IV′ species are assumed to be formed by hydrogen additions to the II and II′ species respectively, and an unpaired electron is denoted by ·. Since the single C–C bond in the IV and IV′ species can rotate during adsorption, the *trans*-1,2-d_2 species can be produced from the I′ species.



The observed difference between the yield of the *trans*-1,2-d_2 and that of the 1,1-d_2 species can now be interpreted by the following reasoning: the former species may be produced from both the adsorbed species, I and I′, but the latter, from only I′.

Quantitative Treatment of the Deuterium Distributions. The proposition presented above may be checked quantitatively, because the relative abundancies of the eight isomeric species of propylene produced are derivable by the use of the following parameters:

$$\left[\underset{*}{H}\right]/\left[\underset{*}{D}\right]=x,\quad \left[CH_3\text{-}\underset{*}{C}=\underset{*}{C}D\right]/\left[CH_3\text{-}\underset{*}{C}=\underset{*}{C}H\right]=y,$$

and;

$$\frac{\text{specific rate of Process (6)}}{\text{specific rate of Process (3)}}=\alpha.$$

Detailed formulae of the relative values for producing each species are shown in Table 5. The relative abundances of the isomeric species of propylene were thus calculated for suitable choices of the values for the parameters (x, y, α). They can be compared with the observed values derived from the fine and hyperfine distributions; those over Pd, Pt, and Ni are shown in Table 6. Over these metals, the methyl group of propylene was not substituted practically by deuterium, as is shown in Table 3. This is the reason why the calculation was carried out in only three metals at first. The degree of agreement between the calculated

Table 5. Relative probability of producing isomeric species of propylene

Species	From $CH_3\text{-}\underset{*}{C}=\underset{*}{C}H$	From $CH_3\text{-}\underset{*}{C}=\underset{*}{C}D$	Total probability
d_3	—	$y\cdot(1+\alpha)$	$y\cdot(1+\alpha)$
c-1,2-d_2	$1+\alpha/2$	$xy\cdot\alpha/2$	$1+(1+xy)\cdot\alpha/2$
t-1,2-d_2	$\alpha/2$	$xy\cdot(1+\alpha/2)$	$xy+(1+xy)\cdot\alpha/2$
1,1-d_2	—	$xy\cdot(1+\alpha)$	$x[y(1+\alpha)]$
2-d_1	$x\cdot(1+\alpha)$	—	$x\cdot(1+\alpha)$
t-1-d_1	$x\cdot(1+\alpha/2)$	$x^2y\cdot\alpha/2$	$x[1+(1+xy)\cdot\alpha/2]$
c-1-d_1	$x\cdot\alpha/2$	$x^2y\cdot(1+\alpha/2)$	$x[xy+(1+xy)\cdot\alpha/2]$
d_0	$x^2\cdot(1+\alpha)$	—	$x[x(1+\alpha)]$

$[\underset{*}{H}]/[\underset{*}{D}]=x$, $[CH_3\text{-}\underset{*}{C}=\underset{*}{C}D]/[CH_3\text{-}\underset{*}{C}=\underset{*}{C}H]=y$, Process (6)/ Process (3)$=\alpha$.

Table 6. Comparison of calculated relative abundance of deuteropropylene species with the observed (70% conv.)

Species	Pd		Pt		Ni		Rh	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
d_3	0.13	0.13	0.16	0.17	1.02	1.02	1.01	1.35
c-1,2-d_2	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
t-1,2-d_2	0.13	0.13	0.20	0.20	0.44	0.44	0.40	0.40
1,1-d_2	0.01	0.01	0.03	0.02	0.28	0.26	0.39	0.39
2-d_1	0.08	0.09	0.11	0.12	0.30	0.30	0.33	0.29
t-1-d_1	0.08	0.08	0.10	0.10	0.24	0.25	0.29	0.29
c-1-d_1	0.01	0.01	0.02	0.02	0.11	0.11	0.13	0.12
d_0	0.01	0.01	0.02	0.01	0.06	0.07	0.12	0.08
x		0.08		0.10		0.25		0.29
y		0.12		0.14		0.86		1.34
α		0.28		0.46		0.67		0.02

and observed values may be satisfactory, especially so in the case of palladium. If the observed ratios of geseous methylacetylene-d_1 to methylacetylene-d_0 are adopted for y, agreement is impossible, suggesting that the rate of the desorption process is very small; therefore, a large difference in the deuterium distributions of methylacetylene may exist between the gas phase and the adsorbed phase over these three metals. On the contrary, the difference is estimated to be small in the cases of Rh and Ru from the fact that $CH_3-C\equiv CD$ was produced in a large amount.

Consequently, the hydrogenation scheme may be expressed well by (3), (4), and (6), especially over nickel, palladium, and platinum. Over iridium, rhodium, and ruthenium, however, the scheme seems somewhat more complicated, because the attempt to obtain a good agreement between theory and experiment failed, in spite of the large variation in x, y, and α parameters. In Table 6, the results for Rh are listed together with those for Ni, Pd, and Pt. This disagreement is probably ascribable to the addition of some other processes, leading to the appearance of highly-deuterated propylenes, which are remarkable over Ir, Rh, and Ru.

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