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HYDROGENATION OF ACETYLENE OVER NICKEL

By

Atsushi TAKEUCHI and Koshiro MIYAHARA*

(Received Sep. 13, 1973)

Abstract

In connection with the mechanistic elucidation of the fact that nickel became highly selective for the partial hydrogenation of acetylene to ethylene by its pretreatment with a trace of sulfur, some basic experiments were carried out by the use of nickel wire as a catalyst. The whole products of acetylene hydrogenation at ca. 120°C were analyzed and their kinetics were investigated between 19 and 115 mmHg of the partial pressures of hydrogen and acetylene.

It was found that the side reactions of the simple hydrogenation of acetylene into C₂ hydrocarbons were the formation of C₄ hydrocarbons and their cracking into methane and propylene. These side reactions were optimal at ca. 75 mmHg of the hydrogen partial pressure. The selectivity of the partial hydrogenation into ethylene and the relative amounts of formed butene isomers were nearly independent upon hydrogen and acetylene partial pressures and, furthermore, upon the addition of 1, 3-butadiene. It was concluded that the step of hydrogen chemisorption may be rate-controlling for all reactions observed, however, above 75 mmHg of hydrogen partial pressure some steps to form free radicals become rate-controlling for the side reactions.

Introduction

Ethylene and ethane are simultaneously formed by acetylene hydrogenation and ethylene formed is converted conclusively into ethane in the presence of nickel catalyst,¹ while ethylene is not hydrogenated further when nickel was treated preliminarily by a trace of sulfur or selenium.² With a few exceptions,³ mechanistic analyses of acetylene hydrogenation into ethylene and ethane catalyzed by metals have ever been carried out⁴,⁵ by a priori neglection of the effect of side reactions, e.g., polymerization of acetylene. The polymerization usually amounts to few tens percents and in some cases beyond a half of acetylene consumed,¹ hence it may affect the mechanism of the simple hydrogenation of acetylene.

In this respect the whole products of acetylene hydrogenation over nickel catalyst were analyzed in the present work, and the results were

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discussed with special reference to the sorts of reaction caused simultaneously in the acetylene hydrogenation and the mechanistic relations among them. This study is basic for the elucidation of the high selectivity of the sulfurated nickel for the partial hydrogenation of acetylene to ethylene.

**Experimental**

**Materials.**

Cylinder hydrogen was purified by passing it through a heated siver-palladium thimble. Pure acetylene and other hydrocarbons from TAKACHIHO Chemical Co. Ltd. was further purified by distillation repeated in vacuum. Catalyst nickel was a wire of 0.1 mm in diameter and 210 m in length and packed in a reaction vessel of ca. 100 ml volume. It was heated before each run of reaction in 1.0 mmHg O₂ at 500°C for 5 min. and then in few tens mmHg H₂ at 300°C for ca. 10 hrs and finally evacuated for 2 hrs at 300°C to have a constant activity. The reaction temperature was fixed at ca. 120°C which was close to the previous one⁵ and made the reaction to proceed with a rate favorable for the analyses of its products.

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**Fig. 1.** Diagram of the reaction apparatus.

Apparatus and procedures.

Fig. 1 shows the apparatus which was a conventional, closed circulation system of ca. 600 ml volume and the whole was made of Pyrex glass. After the activation of catalyst as described above, the reaction was started by introducing a known amount of reaction mixture gas into the reaction system and circulating it at a rate of 1,700 ml/min. A part of gas was sampled at times into sampling vessel, S, and the total pressure was followed by a mercury manometer, M. Catalyst in the reaction vessel, R, was protected from mercury and other contaminations by traps, T₁ and T₂, cooled by dry ice.

Analysis of the products.

Sampled gas was divided into two part for the analyses by two gas-chromatographs with flame ionization detectors; one for C₁ and C₂ hydrocarbons was equipped with a column of silica gel and the other for C₃ and higher hydrocarbons with a column of VZ-7 from Gascho Industrial Co. Ltd. The amounts of components other than butene were determined by taking account of their sensitivities evaluated by the use of respective standard gas samples. The sensitivities of butene isomers were assumed to be the same and corrected with reference to 1-butene.

In the case of deuteration of light acetylene, the relative amounts of H₂, HD and D₂ were first measured by introducing the sampled gas into a mass spectrometer (Hitachi RMU-6) through a liquid nitrogen trap. Hydrocarbons condensed in the trap was then vaporized into the mass spectrometer and the spectrum of ethylene was recorded at ca. 13 volt of the ionization voltage, Vₛ, with which the spectrum exclusively consists of the parent peaks of respective deuterated ethylenes. The vaporized gas was finally admitted into a gaschroma-mass spectrometer and the relative amounts of respective deuterated isomers of acetylene and ethane were measured as usual at 70 volt of Vₛ.

Results

1. Time courses of products.

Figs. 2(a), 2(b) and 3 show the typical time courses of products formed by a run with 19.6 mmHg acetylene and 38.8 mmHg hydrogen. Butane was detected even at the early stage of the reaction. Hydrocarbons higher than C₄ were absent throughout the experiments.

The selectivity of the simple hydrogenation to ethylene and ethane and
Fig. 2. Time courses of the reactants and products of the reaction with 19.6 mmHg acetylene and 38.8 mmHg hydrogen at 118°C.


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Fig. 3. Time course of composition of butene formed by the reaction of Fig. 2. ○: 1-butene, ●: cis-2-butene and △: trans-2-butene. The parenthesized plots gives the composition at the isomerization equilibrium.

that of the partial hydrogenation to ethylene are defined as

\[ S_z = 10^9 P_{c_1} [P_{c_1} + 2(P_{c_3} + P_{c_4})] \]  \hspace{1cm} (1a)

and

\[ S_n = 10^9 P_{C_1}/P_{C_1}, \]  \hspace{1cm} (1b)

respectively, and their time courses in the reaction mentioned above are given in Fig. 4. The quantities, \( P_{c_1}, P_{c_3}, \) and \( P_{c_4} \) in Eqs. (1) are pressures of the total \( C_3, C_4 \) and \( C_4 \) hydrocarbon products, respectively, and \( P_E \) the partial pressure of ethylene.

From these result we see that

i) the simple acetylene hydrogenation was accompanied apparently by four side reactions, that is, dimerization of acetylene, hydrogenation of dimers, isomerization of butenes and hydrocracking of \( C_4 \) hydrocarbons into \( C_1 \) and \( C_3 \) hydrocarbons; the last one was concluded on the basis of the fact of Fig. 2(b) that the amounts of methane and propylene were equal throughout the time course,

ii) hydrogenation of olefins and the isomerization of butenes were suppressed
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Fig. 4. Time courses of the selectivities in the reaction of Fig. 2.

by the presence of acetylene, while 1, 3-butadiene was hydrogenated and
iii) ethane as well as butane was formed even at the very early stage of
acetylene hydrogenation, where $S_E$ was ca. 95%.

In connection with the above results of ii) and iii), a run of reaction
was carried out at 120°C with a mixture of C$_2$H$_4$, C$_2$D$_2$ and D$_2$ at 15.8, 30.9
and 30.9 mmHg, respectively. Ethane formed at 28% conversion of acetylene
was analyzed by gaschroma-mass spectrometer and found to be C$_2$D$_6$ alone.
This fact shows that ethylene in gas phase is not hydrogenated in the
presence of acetylene, hence ethane evolved at the early stage of acetylene
hydrogenation was formed directly from adsorbed acetylene, but not from
ethylene once liberated into gas phase.

In Table 1 the selectivities, $S_2$ and $S_E$, of the present experiments are
compared with those ever observed with supported nickel catalyst$^4$, where
conversion is the percentage of reacted acetylene. $S_2$ is remarkably high
in the present case of nickel wire.
Fig. 5. Dependence on the hydrogen partial pressure of the initial rate of C4 hydrocarbons formation at $P_A=19 \text{ mmHg}$ and 118°C.

Fig. 6. Dependence on the hydrogen partial pressure of the initial rate of ethylene formation at $P_A=19 \text{ mmHg}$ and 118°C.
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Table 1. Comparison of the selectivities given by Eqs. (1a) and (1b)

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Catalyst</th>
<th>Conversion, %</th>
<th>$S_2$, %</th>
<th>$S_6$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present exp.</td>
<td>118 nickel wire</td>
<td>80</td>
<td>87</td>
<td>93</td>
</tr>
<tr>
<td>Sheridan</td>
<td>101 nickel pumice</td>
<td>80</td>
<td>38</td>
<td>85</td>
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</tbody>
</table>

Fig. 7a. Composition of butene isomers formed by the reaction of Fig. 5. ○: 1-butene, ●: cis-2-butene and △: trans-2-butene. The parenthesized plots give the composition at the isomerization equilibrium.
2. Initial rate kinetics.

a) Dependence on hydrogen partial pressure. The initial hydrogen partial pressure, $P_H$, was varied from 19 to 115 mmHg by fixing the initial acetylene pressure, $P_A$, at 19 mmHg. The initial rates were approximated by a time mean of the amounts of respective products formed during the initial 20\% conversion. It is distinguishing that the rate of dimerization as well as propylene formation were decreased, as shown in Fig. 5, by increasing $P_H$ beyond ca. 75 mmHg, whereas the formation rate, $V_E$, of ethylene as well as that of ethane and the rate of the total pressure decrease were increased monotoneously with rise of $P_H$ as shown in Fig. 6. The relative
amounts of respective C₄ hydrocarbons were independent upon \( P_H \) as shown in Figs. 7(a) and 7(b).

b) Dependence on acetylene partial pressure. Every initial rates mentioned above were found to be monotonously decreased with rise of \( P_A \). The relative amounts of respective C₄ hydrocarbons were independent of \( P_A \) and nearly the same as those given in Figs. 7(a) and 7(b).

The partial pressure dependences of the rates are summerized in Table 2. The pressure dependences of \( S_2 \) and \( S_E \) are given in Figs. 8(a) and (b). \( S_E \) is nearly constant independently upon both \( P_H \) and \( P_A \). The change of \( S_2 \)

![Fig. 8](image)

Fig. 8. Partial pressure dependence of the selectivities at the initial stage of acetylene hydrogenation at 118°C. (a): Dependence on \( P_H \) at \( P_A = 19 \text{ mmHg} \).
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Fig. 8. (b): Dependences of $S_E$ and $S_2$ on $P_A$ at $P_H=19$ mmHg.

**Table 2.** Reaction orders of the respective initial formation rates in acetylene hydrogenation at 118°C catalyzed by nickel wire

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Hydrogen</th>
<th>Acetylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total pressure decrease</td>
<td>1.3</td>
<td>-0.2</td>
</tr>
<tr>
<td>Ethylene formation</td>
<td>1.2</td>
<td>-0.3</td>
</tr>
<tr>
<td>Ethane formation</td>
<td>1.4</td>
<td>-0.2</td>
</tr>
<tr>
<td>C$_4$ (total) formation</td>
<td>1.5$^*$</td>
<td>-0.3</td>
</tr>
<tr>
<td>Propylene formation</td>
<td>1.3$^*$</td>
<td>-0.2</td>
</tr>
</tbody>
</table>

* The hydrogen partial pressure was lower than 75 mmHg.
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Fig. 9. The effect of addition of 11.0 mmHg 1,3-butadiene to the reacting mixture of 27.6 mmHg acetylene and 39.1 mmHg hydrogen at 121°C. 1,3-butadiene was added at 124 min of the reaction time.

(a): total pressure, ○: mole % of butene in products.
(b): Composition of butene. ○: 1-butene, ●: cis-2-butene and △: trans-2-butene. The parenthesized plots give the result obtained by the hydrogenation of 1,3-butadiene alone at 121°C.
is mainly due to the dimerization of acetylene being optimal at ca. 75 mmHg of \( P_{\text{II}} \).

c) Activation heats. The initial rates of ethylene, ethane and butene formation from 20 mmHg acetylene and 39 mmHg hydrogen were observed at 86, 96 and 118°C and the activation heats were estimated at 20, 14 and 27 kcal/mole, respectively.

3. Hydrogenation of 1, 3-butadiene.

To elucidate the intermediate of \( \text{C}_4 \) hydrocarbon formation, 1, 3-butadiene was added to the reacting gas of acetylene hydrogenation. In this case traps \( T_1 \) and \( T_2 \) were not cooled to avoid the condensation of butadiene. As shown in Fig. 9(a), butene formation was remarkably accelerated by this addition of 1, 3-butadiene, but the cracking of \( \text{C}_4 \) hydrocarbons was not and the relative amounts of butene isomers were not affected as shown in Fig. 9(b). The result of Fig. 9(b) somewhat differs from that of Fig. 3, probably being due to some change of catalyst activity caused by the traps being not cooled. In the case of hydrogenation of 1, 3-butadiene alone, the cracking was scarce and the isomeric composition of formed butene was considerably different from those in the case of acetylene hydrogenation as shown in Fig. 9(b) with parentheses.

4. Deuteration of acetylene.

Distribution of D atoms in gaseous hydrogen, ethylene and ethane were followed in the course of the reaction of 19.7 mmHg \( \text{C}_2\text{H}_2 \) with 38.0 mmHg \( \text{D}_2 \) at 120°C. Deuterosubstituted acetylene was not formed at all. The results are given in Tables 3 and 4. The relative amounts of deuteroethanes were accompanied by large errors due to a lot of fragmentation in mass spectra and seem to be in random distribution of D atoms similarly to the

| Table 3. The isotopic composition of hydrogen gas formed by the reaction of 19.7 mmHg \( \text{C}_2\text{H}_2 \) with 38.0 mmHg \( \text{D}_2 \) at 120°C catalyzed by nickel wire |
|---|---|---|
| Conversion, % | 21 | 45 | 69 |
| \( \text{H}_2 \) | 0.5 | 0.6 | 1.3 |
| HD | 3.5 | 5.1 | 8.7 |
| \( \text{D}_2 \) | 96.0 | 94.3 | 90.0 |
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Table 4. The relative amounts of deuterosubstituted ethylenes and ethanes formed by the reaction of Table 3. (Parenthesized figures are the relative amounts in the case of the random distribution of D atoms at the observed D atomic fraction)

<table>
<thead>
<tr>
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<th>Conversion, %</th>
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<tbody>
<tr>
<td></td>
<td>21</td>
</tr>
<tr>
<td>C_2H_4</td>
<td>34.7 (21.4)</td>
</tr>
<tr>
<td>C_2H_2D</td>
<td>21.5 (40.2)</td>
</tr>
<tr>
<td>C_2H_2D_2</td>
<td>29.2 (28.4)</td>
</tr>
<tr>
<td>C_2HD_3</td>
<td>11.5 ( 8.9)</td>
</tr>
<tr>
<td>C_2D_4</td>
<td>3.1 ( 1.1)</td>
</tr>
</tbody>
</table>

D atomic fraction 0.318 0.458 0.468

<table>
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<th>Conversion, %</th>
</tr>
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<tr>
<td>C_2H_6</td>
<td>0 ( 0.1)</td>
</tr>
<tr>
<td>C_2H_5D</td>
<td>1 ( 1.1)</td>
</tr>
<tr>
<td>C_2H_4D_2</td>
<td>12 ( 6.3)</td>
</tr>
<tr>
<td>C_2H_3D_2</td>
<td>21 (19.0)</td>
</tr>
<tr>
<td>C_2H_2D_4</td>
<td>21 (32.6)</td>
</tr>
<tr>
<td>C_2HD_5</td>
<td>25 (28.7)</td>
</tr>
<tr>
<td>C_2D_6</td>
<td>20 (11.2)</td>
</tr>
</tbody>
</table>

D atomic fraction 0.695 0.681 0.657

Discussion

Discussion is given first on the sorts of reaction caused by the present catalysis. Ethylene, ethane, 1, 3-butadiene, butenes, butane and equimolar methane and propylene were formed at the early stage of the present reaction. Ethylene, propylene and butenes were not hydrogenated in the presence of acetylene. Accordingly, the following reactions are considered to take place simultaneously as the reaction routes\(^0\) linearly independent of each other.

\[
\begin{align*}
C_2H_2 + H_2 & = C_2H_4, \quad (2 \text{ a}) \\
C_2H_2 + 2H_2 & = C_2H_6, \quad (2 \text{ b}) \\
2C_2H_2 + H_2 & = C_2H_6, \quad (2 \text{ c}) \\
2C_2H_2 + 2H_2 & = C_4H_6, \quad (2 \text{ d})
\end{align*}
\]
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\[2\text{C}_2\text{H}_2 + 3\text{H}_2 = \text{C}_4\text{H}_{10}, \quad (2\ e)\]
\[2\text{C}_2\text{H}_2 + 3\text{H}_2 = \text{CH}_4 + \text{C}_3\text{H}_6. \quad (2\ f)\]

Hydrogenation of 1, 3-butadiene took place in the presence of acetylene as shown in Fig. 3 and formation of butenes was accelerated by the addition of 1, 3-butadiene to the reacting gas of acetylene hydrogenation, whereas the composition of butene isomers remained constant, as shown in Figs. 9. These results suggest that adsorbed 1, 3-butadiene is the starting \(\text{C}_4\) intermediate of \(\text{C}_4\) hydrocarbons formation and the step of 1, 3-butadiene adsorption in the presence of acetylene is considerably reversible as compared with those of olefins. Accordingly, the reactions,

\[\text{C}_4\text{H}_6 + \text{H}_2 = \text{C}_4\text{H}_{10}, \quad (2\ g)\]
\[\text{C}_4\text{H}_6 + 2\text{H}_2 = \text{C}_4\text{H}_{10}, \quad (2\ h)\]

may take place simultaneously with reactions \((2\ d), (2\ e)\) and \((2\ f)\). However, these reactions can be expressed by the linear combinations of \((2\ c), (2\ d)\) and \((2\ e)\) as \((2\ g) = (2\ d) - (2\ c)\) and \((2\ h) = (2\ e) - (2\ c)\). The reaction,

\[\text{C}_4\text{H}_6 + 2\text{H}_2 = \text{CH}_4 + \text{C}_3\text{H}_6,\]

similarly obtainable by the linear combination of \((2\ c)\) and \((2\ f)\), is practically absent as expressed in Result 3.

Hydrogenation of olefins as well as isomerization of butenes are similarly given by the linear combinations of the six reactions, \((2\ a)\) \(\text{etc.}\), but they were practically absent due to the inhibition by acetylene.

Consequently, the six, linearly independent reactions, \((2\ a)\) \(\text{etc.}\), are adequate to express the course of the present acetylene hydrogenation.

The kinetics of the formation rates of ethylene, ethane, \(\text{C}_4\) hydrocarbons and propylene are close to each other as given in Table 2, suggesting that reactions \((2\ a)\) \(\text{etc.}\) are rate-controlled by one and the same step. This step is supposed to be hydrogen adsorption retarded by competitive adsorption of acetylene, in consequence of the rate being nearly first order and a little negative order with respect to \(P_\text{H}\) and \(P_\text{A}\), respectively. According to the formation of deuteroetylles with randomly distributed D atoms in course of the reaction of \(\text{C}_2\text{H}_2\) with \(\text{D}_2\), the hydrogen adsorption is concluded to be dissociative. In the other case where hydrogen adsorption is in equilibrium or gaseous hydrogen is added to hydrocarbons, the formation rate of ethane should be proportional to \(P_\text{H}^2\) against the observed result and, furthermore, \(S_\text{H}\) should depend upon \(P_\text{H}\) as shown by the broken line in
Fig. 8 (a), far differing from the observed result.

The broken line was obtained as follows. As gaseous ethylene was inert in acetylene hydrogenation and ethane was not adsorbed in the presence of ethylene, \( S_E \) is determined by the desorption rate, \( V_d \), of adsorbed ethylene and the unidirectional rate, \( V_h \), of ethane formation. Denoting the activity of adsorbed ethylene by \( a_{E(a)} \), we have

\[
V_d = k_d a_{E(a)} \quad \text{and} \quad V_h = k_h a_{E(a)} P_H,
\]

hence that

\[
S_E = \frac{10^2}{[1 + (k_h/k_d) P_H]}.
\]

The value of \( k_h/k_d \) was estimated at \( 3.2 \times 10^{-3} \) from the result of Fig. 8 (a), where \( S_E = 94.3\% \) at \( P_H = 19 \text{ mmHg} \). Introducing the value of \( k_h/k_d \) into Eq. (3), we have the broken line in Fig. 8.

We now assume that adsorbed hydrogen atoms are added stepwise to adsorbed acetylene to form ethylene and ethane as

\[
\begin{align*}
\text{HC} &= \text{CH} + \text{H} \rightarrow \text{HC} = \text{CH}_2, \\
\text{HC} &= \text{CH}_2 + \text{H} \rightarrow \text{H}_2\text{C} - \text{CH}_2 \rightarrow \text{C}_2\text{H}_4, \\
\text{H}_2\text{C} - \text{CH}_2 + 2\text{H} &\rightarrow \text{H}_2\text{C} - \text{CH}_3 + \text{H} \rightarrow \text{C}_3\text{H}_6,
\end{align*}
\]

where * denotes a chemisorption bond.

Step (4) is then practically irreversible on account of the absence of deuteroustituted acetylene in the reaction of \( \text{C}_2\text{H}_2 \) and \( \text{D}_2 \), whereas the former steps of (5) and (6) might be equilibrated to result in the random distribution of D atoms in gaseous ethylene and ethane. The latter steps of (5) and (6) are irreversible in the presence of acetylene as discussed before.

With respect to the mechanism of formation and cracking of \( \text{C}_4 \) hydrocarbons, we see that their kinetics were remarkably changed at ca. 75 mmHg of \( P_H \) as shown in Fig. 5, whereas the kinetics of the simple hydrogenation as well as the relative amounts of respective \( \text{C}_4 \) hydrocarbons were not changed as shown in Figs. 6 and 7. The relative amounts were not changed also by addition of 1, 3-butadiene to the reacting gas as shown in Fig. 9 (b). On the basis of these facts we conclude that formation of \( \text{C}_3 \) and \( \text{C}_4 \) hydrocarbons at \( P_H \) above 75 mmHg is rate-controlled by a step of formation of \( \text{C}_2 \) intermediate for dimerization or a step of dimerization, but not by the step of hydrogen adsorption or any step following to dimerization.

If the rate is controlled by the dimerization of vinyl radical formed by
step (4), the kinetics of dimerization might be similar to that of the simple hydrogenation as follows. The rate of C₄ hydrocarbon formation is now given as

\[ V_{c_4} = k_C a_{V(a)}^2 = k_C a_{A(a)}^2 a_{H(a)} \propto P_H, \]

because of that the activity of adsorbed acetylene, \( a_{A(a)} \), may be constant on account of the nearly full coverage of the catalyst surface by adsorbed acetylene, \( A(a)'s \), and the activity, \( a_{H(a)} \), of H is proportional to \( P_H^{1/2} \) in this case; \( V(a) \) denotes the adsorbed vinyl radical. The observed kinetics was not the case, hence the \( C_2 \) intermediate for dimerization may differ from vinyl radical. Some authors\(^1\),\(^4\),\(^5\) have proposed the formation of free radical such as

\[ \text{HC} = \text{CH} + \text{H} \longrightarrow \text{HC} - \text{CH}_2, \]  

which dimerizes into \( C_4 \) hydrocarbons or reacts with vinyl radical and/or adsorbed acetylene to form \( C_4 \) hydrocarbon free radical. If so, the result of Fig. 5 suggests that the amount of the free radical decreased with rise of \( P_H \) beyond 75 mmHg, however, the details are not clear for the present. The formation of equimolar methane and propylene at a temperature as low as 118°C suggests\(^8\) the existence of unstable \( C_4 \) free radicals, in agreement with the above mechanism of \( C_4 \) free radical formation.

The value of \( S_z \) is determined conclusively by the ratio of the rate of step (4) to (7). After these steps the simple hydrogenation of acetylene and the side reactions to give \( C_1, C_3 \) and \( C_4 \) hydrocarbons do not include any common step, that is, they are kinetically independent with each other. The conclusion agrees with the constant \( S_z \) and the constant composition of \( C_4 \) hydrocarbons as shown in Figs. 7 and 8.

The results described in Result 3 are interesting with respect to the role of adsorbed 1, 3-butadiene in acetylene hydrogenation. On reference to butene being not hydrogenated in the presence of 1, 3-butadiene,\(^9\) the present results indicate that adsorbed 1, 3-butadiene may be an intermediate of butene formation from acetylene, but not convert into \( C_4 \) free radical which cracks into methane and propylene. The adsorbed state of 1, 3-butadiene or its hydrogenation process to butene should be remarkably affected by the presence of acetylene because of the isomeric composition of butene being different from that in the case of hydrogenation of 1, 3-butadiene alone.
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Acknowledgement

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