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HYDROGENATION OF ACETYLENE OVER NICKEL

By

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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 out^{1,4,5)} by *a priori* neglect 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 silver-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 one²⁾ and made the reaction to proceed with a rate favorable for the analyses of its products.

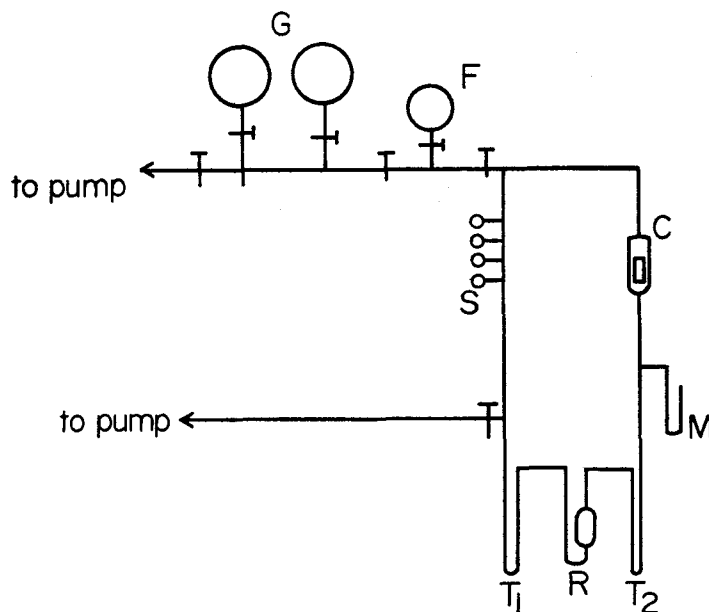


Fig. 1. Diagram of the reaction apparatus.

G: reservoirs of reactant gases, F: reservoir of reactant gas mixture, C: circulation pump, M: mercury manometer, R: reaction vessel, T₁ and T₂: dry ice traps.

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 Gaschro 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, V_e , with which the spectrum exclusively consists of the parent peaks of respective deuteriosubstituted ethylenes. The vaporized gas was finally admitted into a gaschro-mass spectrometer and the relative amounts of respective deuteriosubstituted isomers of acetylene and ethane were measured as usual at 70 volt of V_e .

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

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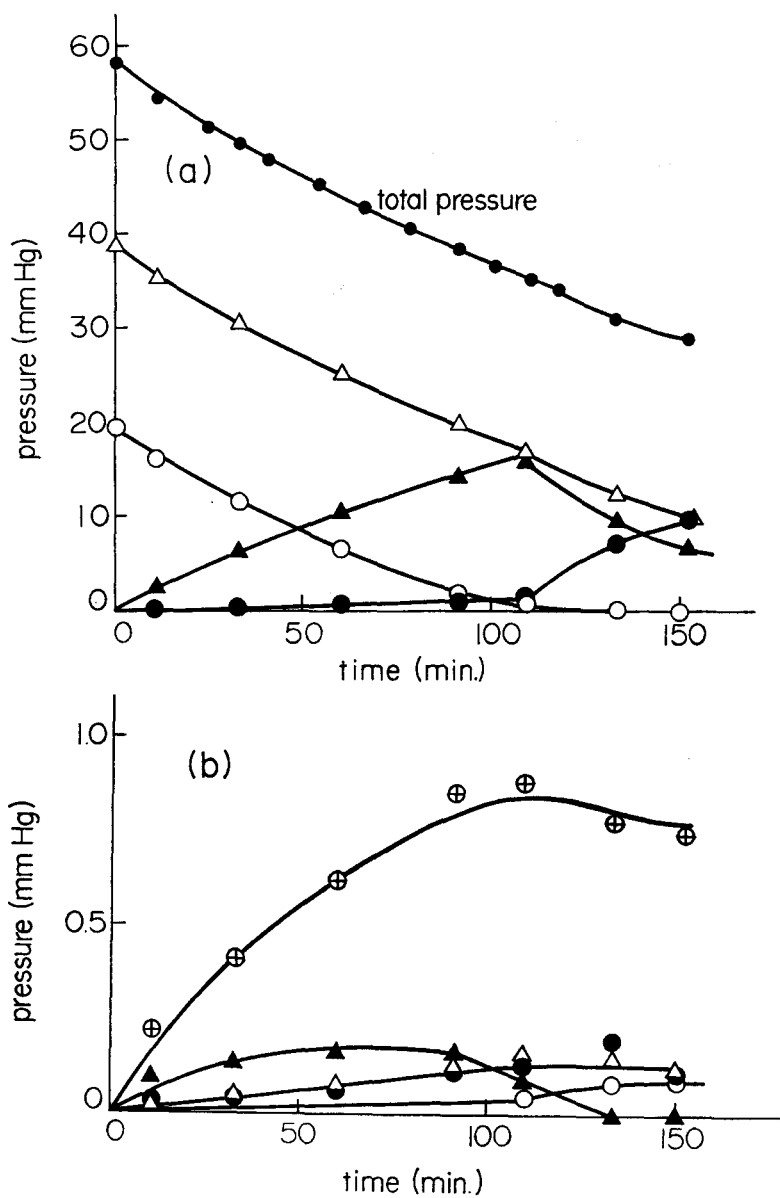


Fig. 2. Time courses of the reactants and products of the reaction with 19.6 mmHg acetylene and 38.8 mmHg hydrogen at 118°C.

- (a): Reactants and C₂ hydrocarbons. Δ : hydrogen, \circ : acetylene, \blacktriangle : ethylene and \bullet : ethane.
 (b): C₄ hydrocarbons. \oplus : butene in total, \blacktriangle : 1,3-butadiene, \circ : n-butane, \triangle : propylene and \bullet : methane.

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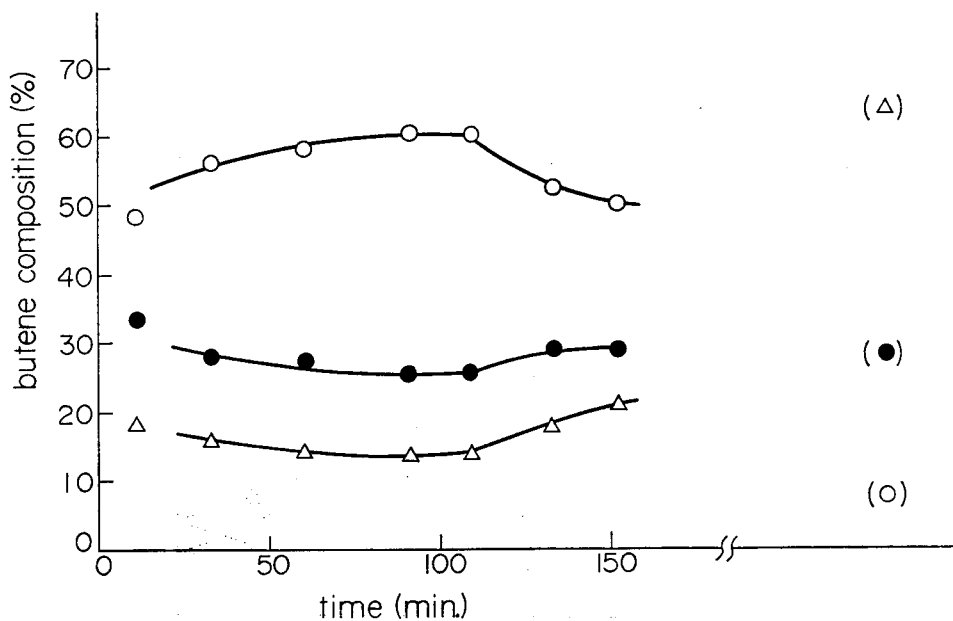


Fig. 3. Time course of composition of butene formed by the reaction of Fig. 2. ○ : 1-butene, ● : *cis*-2-butene and △ : *trans*-2-butene. The parenthesized plots gives the composition at the isomerization equilibrium.

that of the partial hydrogenation to ethylene are defined as

$$S_2 = 10^2 P_{C_2} / [P_{C_2} + 2(P_{C_3} + P_{C_4})] \quad (1a)$$

and

$$S_E = 10^2 P_E / P_{C_2}, \quad (1b)$$

respectively, and their time courses in the reaction mentioned above are given in Fig. 4. The quantities, P_{C_2} , P_{C_3} and P_{C_4} in Eqs. (1) are pressures of the total C_2 , C_3 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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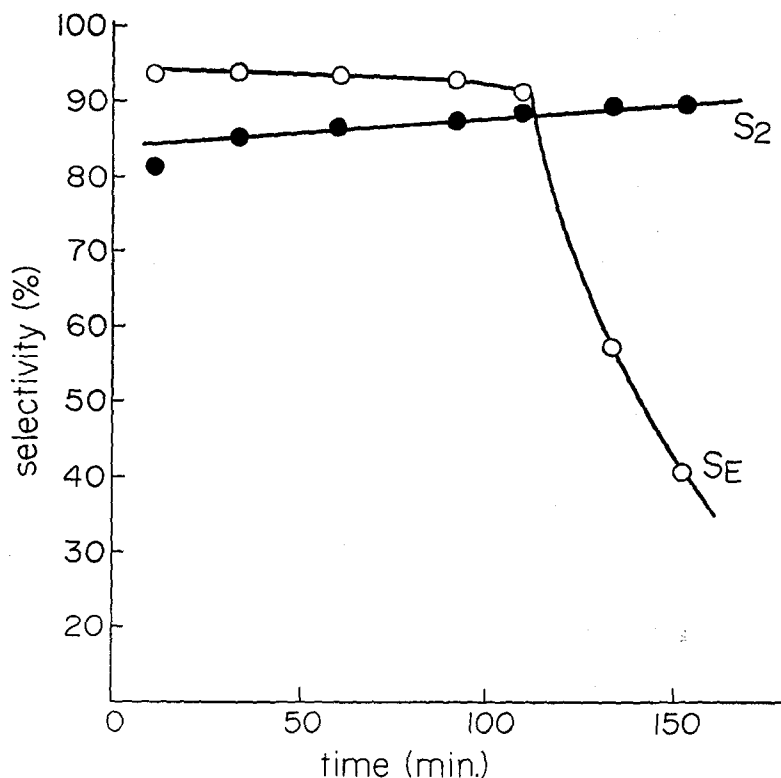


Fig. 4. Time courses of the selectivities in the reaction of Fig. 2.

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_2H_4 , C_2D_2 and D_2 at 15.8, 30.9 and 30.9 mmHg, respectively. Ethane formed at 28% conversion of acetylene was analyzed by gaschromatography and found to be C_2D_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 catalyst⁴⁾, where conversion is the percentage of reacted acetylene. S_2 is remarkably high in the present case of nickel wire.

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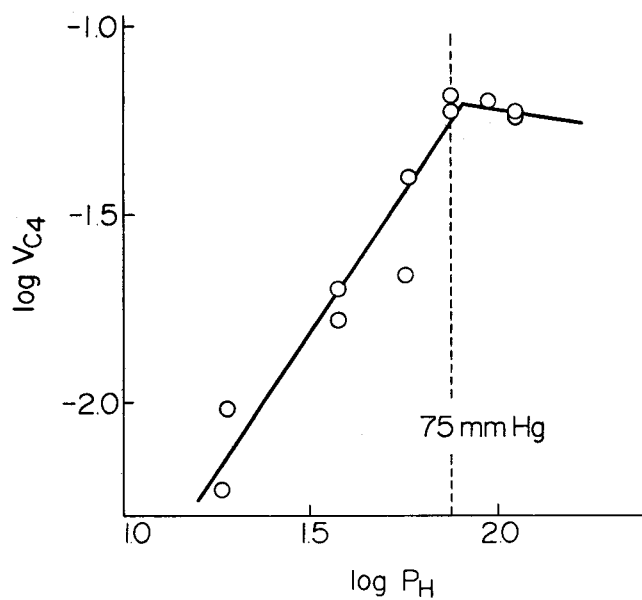


Fig. 5. Dependence on the hydrogen partial pressure of the initial rate of C₄ hydrocarbons formation at $P_A=19$ mmHg and 118°C.

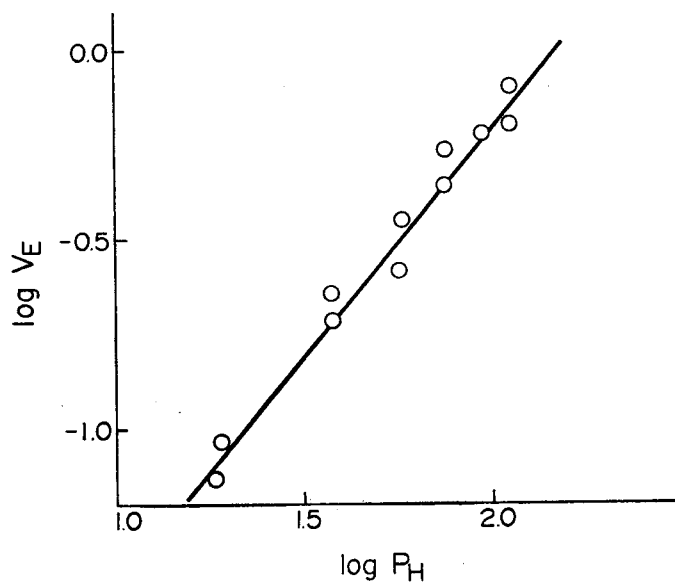


Fig. 6. Dependence on the hydrogen partial pressure of the initial rate of ethylene formation at $P_A=19$ mmHg and 118°C.

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TABLE 1. Comparison of the selectivities given by Eqs. (1 a) and (1 b)

	Temp. °C	Catalyst	Conversion, %	S_2 , %	S_E , %
Present exp.	118	nickel wire	80	87	93
Sheridan ⁴	101	nickel pumice	80	38	85

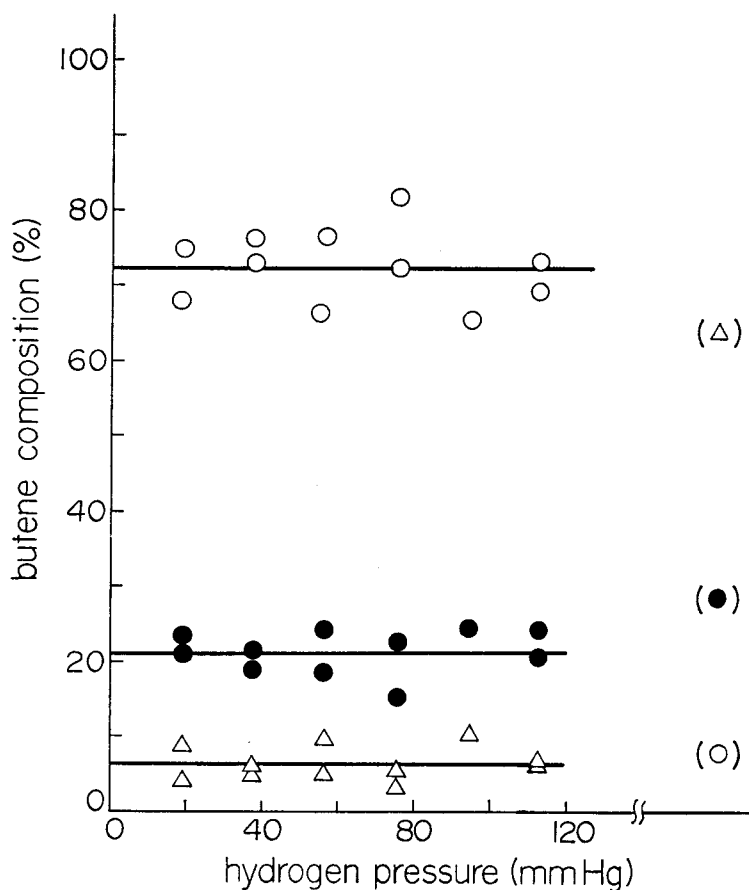


Fig. 7 a. Composition of butene isomers formed by the reaction of Fig. 5. ○: 1-butene, ●: *cis*-2-butene and △: *trans*-2-butene. The parenthesized plots give the composition at the isomerization equilibrium.

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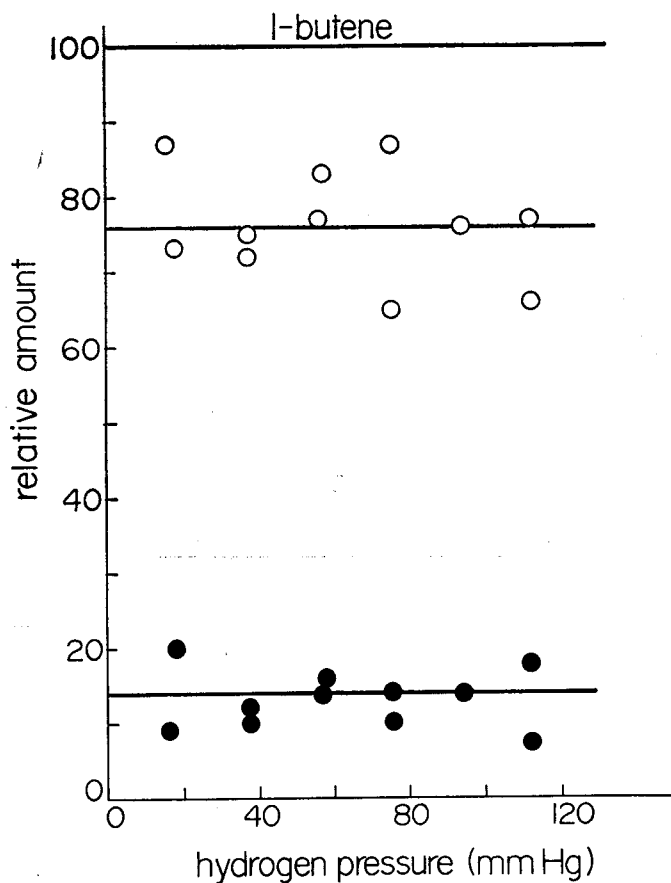


Fig. 7b. The amounts of 1,3-butadiene (○) and *n*-butane (●) relative to that of 1-butene formed by the reaction of Fig. 5.

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 monotonously with rise of P_H as shown in Fig. 6. The relative

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amounts of respective C_4 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 C_4 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 summarized 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

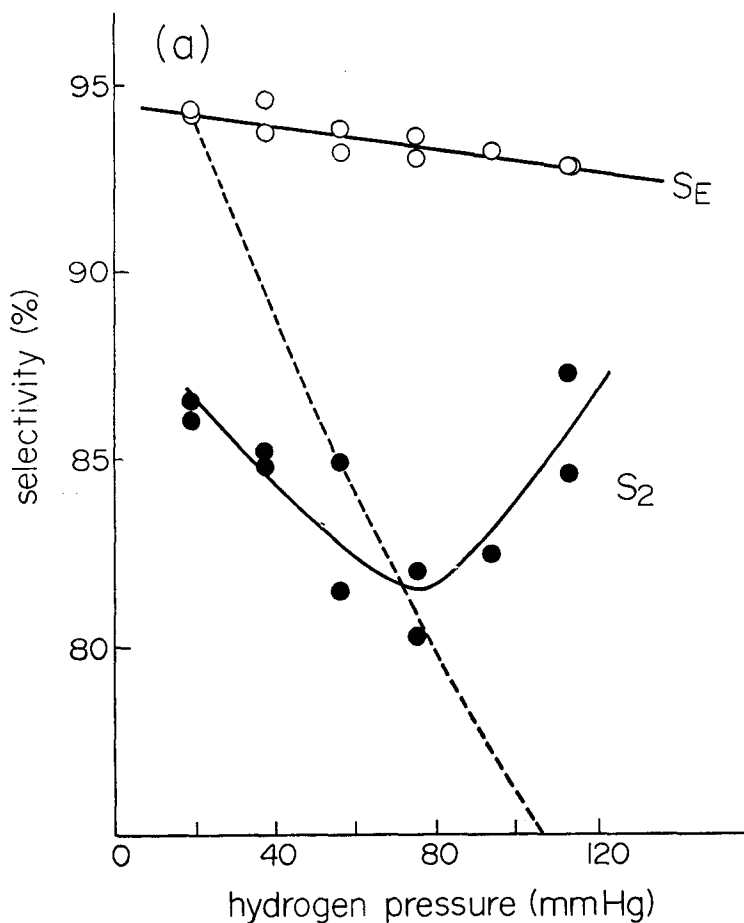


Fig. 8. Partial pressure dependence of the selectivities at the initial stage of acetylene hydrogenation at 118°C.
 (a): Dependence on P_H at $P_A=19$ mmHg.

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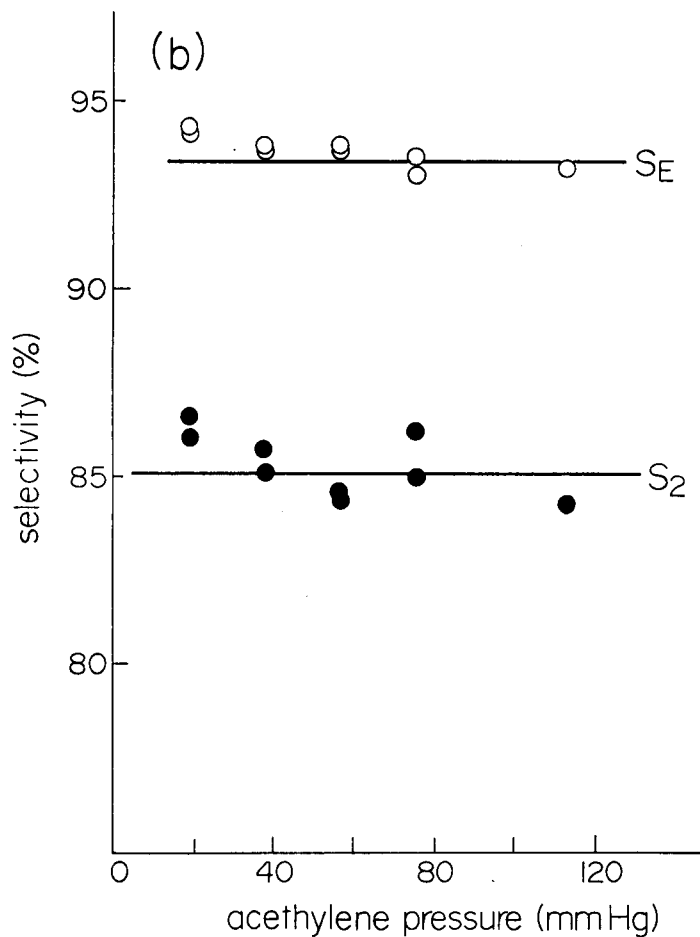


Fig. 8. (b): Dependences of S_E and S_2 on P_A at $P_H=19$ mmHg.

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

Reaction	hydrogen	acetylene
Total pressure decrease	1.3	- 0.2
Ethylene formation	1.2	- 0.3
Ethane formation	1.4	- 0.2
C_4 (total) formation	1.5*	- 0.3
Propylene formation	1.3*	- 0.2

* The hydrogen partial pressure was lower than 75 mmHg.

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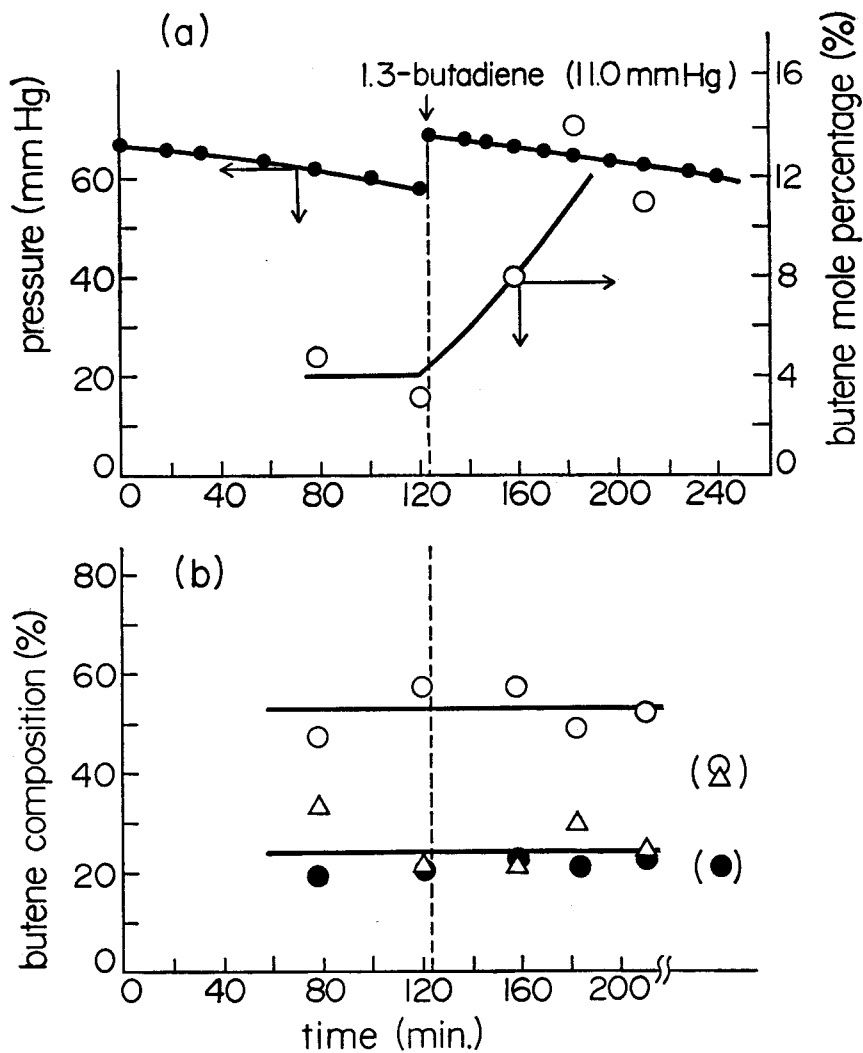


Fig. 9. The effect of addition of 11.0 mmHg 1,3-butadiene to the reacting mixture of 27.6 mmHg acetylene and 39.1 mmHg hydrogen at 121°C. 1,3-Butadiene was added at 124 min of the reaction time.

- (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_{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 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 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 C_2H_2 with 38.0 mmHg D_2 at 120°C. Deuterated acetylene was not formed at all. The results are given in Tables 3 and 4. The relative amounts of deuterioethanes 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 C_2H_2 with 38.0 mmHg D_2 at 120°C catalyzed by nickel wire

	Conversion, %		
	21	45	69
H_2	0.5	0.6	1.3
HD	3.5	5.1	8.7
D_2	96.0	94.3	90.0

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TABLE 4. The relative amounts of deuterio-substituted 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)

	Conversion, %		
	21	45	69
C ₂ H ₄	34.7 (21.4)	9.0 (8.5)	8.7 (7.9)
C ₂ H ₃ D	21.5 (40.2)	30.4 (29.0)	29.4 (28.0)
C ₂ H ₂ D ₂	29.2 (28.4)	36.6 (37.0)	36.0 (37.2)
C ₂ HD ₃	11.5 (8.9)	16.7 (21.0)	18.3 (22.0)
C ₂ D ₄	3.1 (1.1)	7.3 (4.5)	7.6 (4.9)
D atomic fraction	0.318	0.458	0.468
C ₂ H ₆	0 (0.1)	0 (0.1)	0 (0.1)
C ₂ H ₅ D	1 (1.1)	3 (1.3)	6 (1.9)
C ₂ H ₄ D ₂	12 (6.3)	10 (7.1)	13 (9.0)
C ₂ H ₃ D ₃	21 (19.0)	21 (20.4)	19 (22.9)
C ₂ H ₂ D ₄	21 (32.6)	24 (32.8)	22 (32.9)
C ₂ HD ₅	25 (29.7)	25 (28.2)	24 (25.2)
C ₂ D ₆	20 (11.2)	17 (10.1)	16 (8.0)
D atomic fraction	0.695	0.681	0.657

case of deuterioethylenes.

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 routes⁶⁾ linearly independent of each other.



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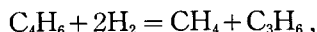
Hydrogenation of 1, 3-butadiene took place in the presence of acetylene as shown in Fig. 3 and formation of butenes was accelerated by the addition of 1, 3-butadiene to the reacting gas of acetylene hydrogenation, whereas the composition of butene isomers remained constant, as shown in Figs. 9. These results suggest that adsorbed 1, 3-butadiene is the starting C_4 intermediate of 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,



and



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 $(2\text{ g}) = (2\text{ d}) - (2\text{ c})$ and $(2\text{ h}) = (2\text{ e}) - (2\text{ c})$. The reaction,



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) *etc.*, but they were practically absent due to the inhibition by acetylene.

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

The kinetics of the formation rates of ethylene, ethane, C_4 hydrocarbons and propylene are close to each other as given in Table 2, suggesting that reactions (2 a) *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_{H} and P_{A} , respectively. According to the formation of deuterioethylenes with randomly distributed D atoms in course of the reaction of C_2H_2 with 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_{H}^2 against the observed result and, furthermore, S_{E} should depend upon P_{H} as shown by the broken line in

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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,⁷⁾ 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

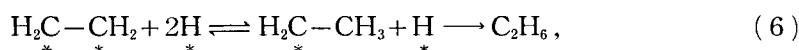
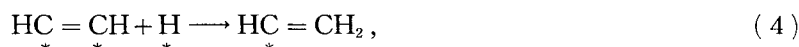
$$V_d = k_d a_{E(a)} \quad \text{and} \quad V_h = k_h a_{E(a)} P_H,$$

hence that

$$S_E = 10^2 / [1 + (k_h/k_d) P_H]. \quad (3)$$

The value of k_h/k_d was estimated at 3.2×10^{-3} from the result of Fig. 8(a), where $S_E = 94.3\%$ at $P_H = 19$ 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



where * denotes a chemisorption bond.

Step (4) is then practically irreversible on account of the absence of deuterium-substituted acetylene in the reaction of C_2H_2 and 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 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 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 C_3 and C_4 hydrocarbons at P_H above 75 mmHg is rate-controlled by a step of formation of 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

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step (4), the kinetics of dimerization might be similar to that of the simple hydrogenation as follows. The rate of C_4 hydrocarbon formation is now given as

$$V_{C_4} = k_{C_4} a_{V(a)}^2 = k_{C_4} a_{A(a)}^2 a_{H(a)}^2 \propto P_H,$$

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



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 suggests⁸⁾ the existence of unstable C_4 free radicals, in agreement with the above mechanism of C_4 free radical formation.

The value of S_2 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_E 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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