# Shock Tube Study on the Mechanism of Hydrogenation and Pyrolysis of Acetylene

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Mixtures of acetylene and deuterium have been subjected to shock heating in a single-pulse shock tube in the temperature range 1000—1600 K. The reaction products were quite the same as those obtained from the pyrolysis of acetylene alone, with a considerable increase in the yields of the minor products. The predominance of 1-buten-3-yne formation and no appreciable dependence of its rate on the concentration of deuterium suggest that the initiation step is the same as that proposed in the pyrolysis of acetylene by itself, *viz.* $2C_2H_2 \rightarrow C_4H_3+H$, the initiation step of the bimolecular reaction of $C_2H_2$ with $D_2$ not being important. A complementary analysis of the isotopic distributions of 1-buten-3-yne, ethylene, and acetylene shows that hydrogenation also occurs by a free-radical chain mechanism, and the $C_4H_3$ radical and H atom generated by the initiation step are mainly responsible for the formation of1-buten-3-yne and ethylene, respectively. The ethylene formation was of first-order in both acetylene and deuterium, and the second-order rate constant was obtained as

$$k(\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = (4.9\pm1.3)\times10^{11}\exp((-34900\pm600)/RT).$$

The hydrogenation of acetylene has been studied by several investigators.[1-6] Skinner and co-workers aimed at clarifying the pyrolysis of ethylene.[2,3] Benson and Haugen, in an attempt to estimate the elementary reaction rate constants of radical reactions which might participate in the pyrolysis of the unsaturated hydrocarbons,[4] made a kinetic analysis of the hydrogenation of acetylene, and concluded that a free-radical chain mechanism should predominate. Skinner *et al.* showed that $C_2H_3D$ is the most abundant among the ethylene isomers produced in the shock heated mixture of acetylene and deuterium. The result is in line with the prediction from the free-radical chain mechanism proposed by Benson and Haugen. In their scheme the chain propagation is initiated by the bimolecular reaction of acetylene and deuterium, $C_2H_2+D_2 \rightarrow C_2H_2D+D$.

On the other hand, the effects of added hydrogen on the yields of the pyrolysis products were extensively examined in static and flow systems.[7-10] It was shown that the addition of hydrogen has little influence on the yields of the major products of the pyrolysis.

The pyrolysis of acetylene proceeds *via* the free-radical chain mechanism initiated by the bimolecular reaction of acetylene,[11] $2C_2H_2 \rightarrow C_4H_3+H$. The H atom produced by the initiation step can lead to the formation of ethylene as well as 1-buten-3-yne in the presence of hydrogen. When deuterium instead of hydrogen is added, the product distribution and isotopic distribution can be utilized for clarifying the mechanisms of the pyrolysis and hydrogenation of acetylene.

## Experimental

*Apparatus and Procedure.* The hydrogenation and pyrolysis of acetylene in the presence of deuterium was studied in a 4-cm single-pulse shock tube, the length of the driven section being 277 cm long, and that of the driver section adjustable but fixed at 157 cm. The design and operation of the shock tube were reported previously.[11,12]

The driver section was isolated from the pump when the vacuum of the tube reached below $10^{-3}$ Torr, and then filled with the driver gas at about 2 atm of pressure in order to optimize the rupture of the diaphragms by the needle. The driven section was further pumped to a vacuum better than $10^{-4}$ Torr before each run. The leak plus outgassing rate was measured by a cathode ionization gauge immediately after the isolation of the tube from the pump, $6\times10^{-5}$ Torr per minute being obtained. Helium was used as the driver gas. The shocks were fired within 5 min after the driven section had been filled with test gases.

*Materials.* Three different mixtures with the composition of $C_2H_2/D_2/Ar=10/10/80$; 5/10/85; and 10/5/85 were prepared in a 5-l glass vessel and allowed to stand for at least one day before use.

Acetylene(Matheson Co.) was washed with concd sulforic acid and dried through a soda lime tower and then purified by bulb-to-bulb vacuum distillation. Deuterium (Showa Denko Co., 99.5% D atom) and argon (Nippon Sanso Co., nominal purity of 99.9995%) were used without further purification.

A variety of pure gas mixtures with the desired concentrations were prepared for the calibration of the gas chromatography. Argon was also used as the diluent.

1-Buten-3-yne and 1,3-butadiyne synthesized in a pyrolysis experiment were used. The other pure gases (Takachiho Shoji Co., research grade) were used as received.

*Analytical.* The shock heated sample was introduced into 60-ml volume bulb, and analyzed by gas chromatography. Details of the gas chromatographic analysis were reported.[11]

The isotopic distributions of acetylene, 1-buten-3-yne, and ethylene were determined with a Hitachi Model RM-50 mass spectrometer. Acetylene and ethylene were separated on a 3 mm×2 m Porapak T column at 50 °C with helium as the carrier. Each gas component was collected in a trap cooled by liquid nitrogen. The cooled trap was then evacuated for several minutes to remove the carrier gas and contaminants, especially nitrogen and oxygen.

For the measurement of mass spectra of ethylene isomers, the ionization potential was maintained at *ca.* 12 eV to simplify the fragmentation patterns, in which only the parent peaks of the isomers appeared in the mass spectra. The influence of nitrogen and oxygen on $m/e=28$ and 32 in the mass spectra, respectively, can be neglected at a low ionization potential. The mass spectra of 1-buten-3-yne and acetylene isomers were measured at an ionization potential of 50 eV. The method of mass spectral analyses for acetylene and 1-buten-3-yne isomers was described elsewhere.

## Results

Three mixtures were heated behind the reflected shock waves in the temperature range 1000—1600 K. The total densities behind the reflected shock waves were maintained within $(2.35\pm0.11)\times10^{-5}$ mol/cm$^3$, which were the same as those in the pyrolysis experiment in the absence of deuterium.

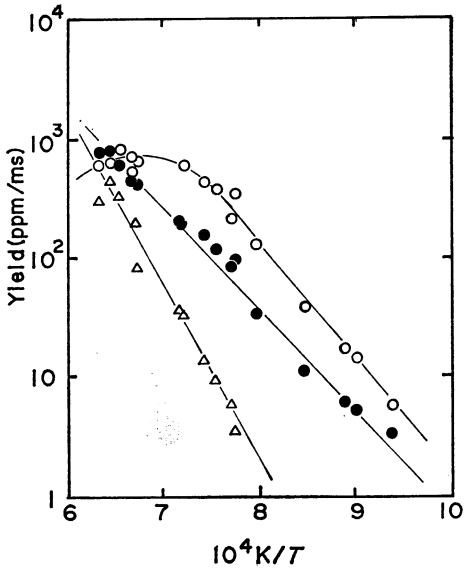


Fig. 1. Major product distribution as a function of temperature($C_2H_2/D_2/Ar=5/10/85$).
○; 1-Buten-3-yne, ●; ethylene, △; 1,3-butadiyne.

*Major Products.* The shock heated gas samples were analyzed by gas chromatography. The analytical results in the case of the mixture with the ratio of $C_2H_2/D_2/Ar$ equal to 5/10/85 are shown in Fig. 1. The major products were 1-buten-3-yne, ethylene, and 1,3-butadiyne in the decreasing order of amount, 1-buten-3-yne and 1,3-butadiyne being the major products of the pyrolysis of acetylene by itself. This indicates that under the present experimental conditions the hydrogenation of acetylene occurs simultaneously with the pyrolysis of acetylene, and in the temperature range up to 1400 K the formation of 1-buten-3-yne dominates that of ethylene.

*1-Buten-3-yne and 1,3-Butadiyne*: As shown in Fig. 1, the yields of 1-buten-3-yne and 1,3-butadiyne as a function of temperature are similar to those of the pyrolysis in the absence of deuterium. The concentration of 1-buten-3-yne also reaches maximum at *ca.* 1500 K.

The effects of added deuterium on the production of 1-buten-3-yne and 1,3-butadiyne for the three mixtures are shown in Figs. 2 and 3, respectively. We see that the yields of 1-buten-3-yne and 1,3-butadiyne seem to be entirely dependent on the initial acetylene concentration, and are little affected by that of deuterium. The rate (yield expressed in ppm/ms) of 1-buten-3-yne formation is approximately of second-order with respect to acetylene, which is the same as that in the $C_2H_2$–Ar system. The second-order rate expression fits the

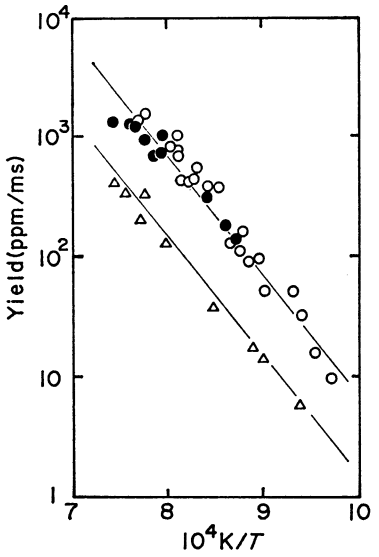


Fig. 2. Effect of deuterium on the 1-buten-3-yne formation.
○; $C_2H_2/D_2/Ar=10/10/80$, △; $C_2H_2/D_2/Ar=5/10/85$, ●; $C_2H_2/D_2/Ar=10/5/85$.

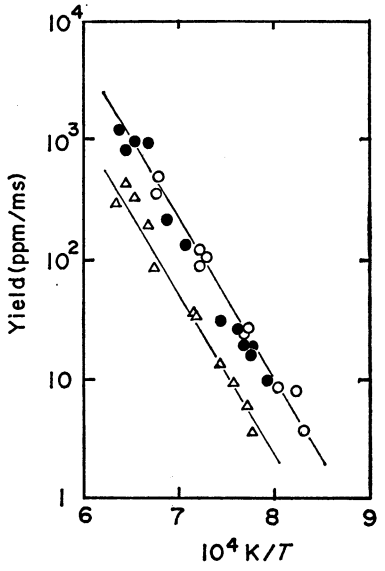


Fig. 3. Effect of deuterium on the 1,3-butadiyne formation.
○; $C_2H_2/D_2/Ar=10/10/80$, △; $C_2H_2/D_2/Ar=5/10/85$, ●; $C_2H_2/D_2/Ar=10/5/85$.

data obtained below 1350 K (41 points) by the least-squares method:

$$k_1(\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = (14.8\pm1.8)\times10^{13} \times \exp((-44200\pm1500)/RT), \quad (1)$$

where the activation energy is expressed in cal*/mol, the errors denoting the standard deviation of the least-squares method.

In order to confirm the effects of deuterium added, the isotopic distribution of 1-buten-3-yne was determined by mass spectrometry. The mass spectral

* 1 $cal_{th}$=4.184 J.

Table 1. Isotopic distributions of 1-buten-3-yne and acetylene

| $T_5$/K[a] | 1205 | 1245 | 1296 | 1371 | 1312[h] | 1290 | 1322 |
|---|---|---|---|---|---|---|---|
| $C_4H_4$[b] | 1.000 | 0.994 | 0.938 | 0.720 | 1.000 | 0.812 | 0.734 |
| $C_4H_3D$ | —[g] | 0.006 | 0.054 | 0.255 | — | 0.188 | 0.239 |
| $C_4H_2D_2$ | — | — | 0.008 | 0.018 | — | — | 0.019 |
| $C_4HD_3$ | — | — | — | 0.007 | — | — | 0.008 |
| $C_4D_4$ | — | — | — | — | — | — | — |
| $C_2H_2$[c] | 0.996 | 0.981 | 0.959 | 0.896 | 0.979 | 0.933 | 0.912 |
| $C_2HD$ | 0.004 | 0.014 | 0.034 | 0.093 | 0.019 | 0.053 | 0.078 |
| $C_2D_2$ | — | 0.005 | 0.007 | 0.011 | 0.002 | 0.014 | 0.010 |
| $[C_4H_4]$[d] | 447 | 834 | 1582 | 2165 | 1281 | 348 | 365 |
| $\tau$/μs[e] | 650 | 710 | 690 | 780 | 690 | 820 | 840 |
| $C_2H_2/D_2$[f] | 10/10 | 10/10 | 10/10 | 10/10 | 10/5 | 5/10 | 5/10 |

a) $T_5$ is the temperature behind the reflected shock wave. b), c) The total amounts of 1-buten-3-yne and acetylene are taken to be equal to 1.000. d) Total yield of 1-buten-3-yne isomers expressed in ppm/ms. e) $\tau$ is the dwell time. f) Composition of the mixture. g) Undetectable. h) Deuterated 1-buten-3-ynes are not detected at 1290 and 1340 K in the mixture of $C_2H_2/D_2=10/5$.

analyses of the 1-buten-3-ynes together with the acetylenes were carried out for several samples taken out of the three mixtures. The results are summarized in Table 1. No appreciable amount of deuterium-substituted 1-buten-3-ynes is formed at lower temperatures. No detectable amount of deuterated 1-buten-3-ynes is observed in the case of the mixture with the composition $C_2H_2/D_2/Ar=10/5/85$. The effect of added deuterium (hydrogen) on the formation of 1-buten-3-yne is small.

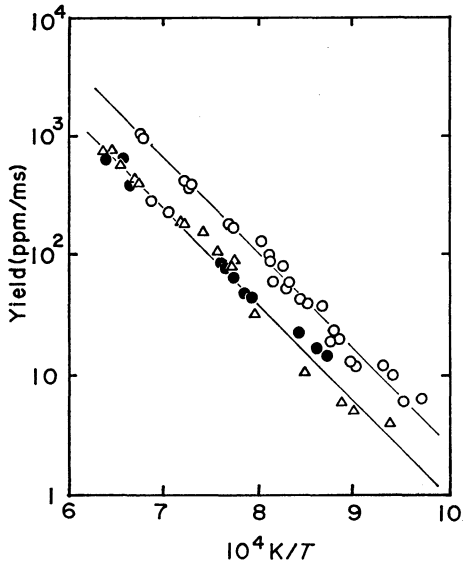


Fig. 4. Concentration dependence of the ethylene formation.
○; $C_2H_2/D_2/Ar=10/10/80$, △; $C_2H_2/D_2/Ar=5/10/85$, ●; $C_2H_2/D_2/Ar=10/5/85$.

*Ethylene*: Although the formation of ethylene was not the predominant reaction under the present experimental conditions, the yield of ethylene remarkably increased in the presence of deuterium.

The yield of ethylene is plotted against the reciprocal of the reaction temperature in Fig. 4. The dependence of the rate on the concentrations of acetylene and deuterium is approximately equal, being approximately of first-order with respect to acetylene and deuterium. Assuming that the rate equation has the form $d[\text{total ethylene}]/dt=k_2[C_2H_2][D_2]$, the second-order rate constant was obtained by the least-squares method:

$$k_2(\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = (4.9\pm1.3)\times10^{11} \times \exp((-34900\pm600)/RT). \quad (2)$$

The isotopic distribution of ethylene was determined by mass spectrometry for several samples out of the shock heated mixture of 10% $C_2H_2$ and 10% $D_2$ in argon. The results of the mass spectral analyses are given in Table 2. We see that $C_2H_3D$ is the most abundant species among the ethylene isomers. Considerable amounts of $C_2H_2D_2$ and $C_2H_4$ are produced.

Table 2. Isotopic distribution of ethylene

| $T_5$/K[a] | 1271 | 1313 | 1388 | 1407 | 1480 |
|---|---|---|---|---|---|
| $C_2H_4$[b] | 0.158 | 0.111 | 0.149 | 0.141 | 0.187 |
| $C_2H_3D$ | 0.709 | 0.744 | 0.653 | 0.661 | 0.487 |
| $C_2H_2D_2$ | 0.121 | 0.131 | 0.169 | 0.176 | 0.258 |
| $C_2HD_3$ | 0.008 | 0.011 | 0.019 | 0.016 | 0.060 |
| $C_2D_4$ | 0.004 | 0.003 | 0.010 | 0.006 | 0.008 |
| $\tau$/μs[c] | 920 | 940 | 930 | 800 | 780 |
| $C_2H_2/D_2$[d] | 10/10 | 10/10 | 10/10 | 10/10 | 10/10 |

a) $T_5$ is the temperature behind the reflected shock wave. b) The total amount of ethylene isomers is taken to be equal to 1.000. c) $\tau$ is the dwell time. d) Composition of the mixture.

*Minor Products.* Methane, ethane, allene, propyne, and 1,3-butadiene were detected as minor products. Although all of them are observed in the pyrolysis of acetylene alone, their yields as a function of temperature differ from those in the case of the $C_2H_2$–Ar system. The yields, especially that of 1,3-butadiene, considerably increased in the presence of deuterium.

The influence of the addition of deuterium to acetylene system on the yields of 1,3-butadiene and methane is shown in Figs. 5 and 6, respectively. The yields of 1,3-butadiene and methane are dependent on both acetylene and deuterium concentrations, those of allene and propyne showing a similar dependence on concentration. This distinct dependence of the minor product yields on the deuterium concentration suggests that they are

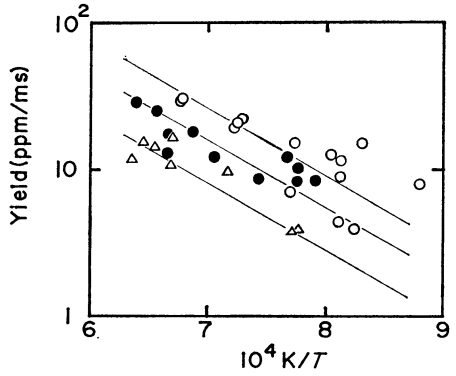


Fig. 5. Effect of deuterium on the 1,3-butadiene formation.
○; $C_2H_2/D_2/Ar=10/10/80$, △; $C_2H_2/D_2/Ar=5/10/85$, ●; $C_2H_2/D_2/Ar=10/5/85$.

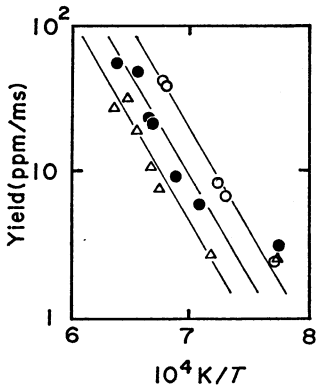


Fig. 6. Effect of deuterium on the methane formation.
○; $C_2H_2/D_2/Ar=10/10/80$, △; $C_2H_2/D_2/Ar=5/10/85$, ●; $C_2H_2/D_2/Ar=10/5/85$.

formed by different paths from those in the $C_2H_2$–Ar system. Thus the direct participation of deuterium in their formation reactions appears evident.

## Discussion

*Mechanism of Ethylene and 1-Buten-3-yne Formation.* The formation of 1-buten-3-yne was the predominant reaction, the shape of the yield-temperature plots for 1-buten-3-yne not being affected by the addition of deuterium. The dependence of rate on the concentration of acetylene was the same as that observed in the pyrolysis of acetylene by itself, deuterium being a negligible effect on the production rate of 1-buten-3-yne. This suggests that the mechanism of 1-buten-3-yne formation is the same as that proposed for the pyrolysis of acetylene in the $C_2H_2$–Ar system. The scheme is represented as follows:[11]

$$2C_2H_2 \longrightarrow C_4H_3 + H, \quad (3)$$

$$H + C_2H_2 \longrightarrow C_2H_3, \quad (4)$$

$$C_2H_3 + C_2H_2 \longrightarrow C_4H_4 + H, \quad (5)$$

$$C_4H_3 + C_2H_2 \longrightarrow C_6H_5, \quad (6)$$

$$C_6H_5 + C_2H_2 \longrightarrow C_4H_4 + C_4H_3. \quad (7)$$

The yield of ethylene increases markedly in the presence of deuterium. If the addition of deuterium to acetylene occurred by a molecular mechanism, $C_2H_2D_2$ would be expected primarily among the ethylene isomers. However, actually $C_2H_3D$ was produced in a large amount. The isotopic distribution obtained in the present analysis is in line with that obtained by Skinner *et al.*,[3] who supported a free-radical chain mechanism for the formation of ethylene.

In the temperature range up to 1400 K, the formation of 1-buten-3-yne is predominant. The initiation step for the formation of ethylene is expected to be the same as that for the production of 1-buten-3-yne. In the above mechanism, Reactions 3 and 4 should be responsible for the formation of ethylene. The scheme of ethylene production is thus completed by the following reactions:

$$C_2H_3 + H_2 \longrightarrow C_2H_4 + H, \quad (8)$$

$$2C_2H_3 \longrightarrow C_4H_6, \quad (9)$$

$$H + C_2H_3 \longrightarrow C_2H_4. \quad (10)$$

The recombination of H atoms with argon as a third body is a relatively slow process and could be neglected. For the sake of simplicity, hydrogen, instead of deuterium, is considered, only bimolecular recombination reactions being taken into account in Reactions 9 and10.

Against the initiation Reaction 3, an alternative initiation step was proposed for the hydrogenation of acetylene:[4]

$$C_2H_2 + H_2 \longrightarrow C_2H_3 + H. \quad (11)$$

Reactions 3 and 11 would compete with each other. When Reaction 11 becomes predominant in the $C_2H_2$–$H_2$ system, 1-buten-3-yne should be formed by the subsequent Reactions 4 and 5. Assuming steady-state concentrations of H atom and $C_2H_3$ radical in the above mechanism with the termination of Reaction 9, the steady-state rate of 1-buten-3-yne formation is given by

$$d[C_4H_4]/dt = k_5(k_{11}/k_9)^{1/2}[C_2H_2]^{3/2}[H_2]^{1/2}. \quad (12)$$

The same concentration dependence of the rate of 1-buten-3-yne generation is also derived in the case of the termination of Reaction 10. Equation 12 shows that the yield of 1-buten-3-yne in the $C_2H_2$–$H_2$ system should be dependent on the concentration of hydrogen, which is in conflict with the observed dependence on the concentration of deuterium.

Another support for the insignificance of Reaction 11 may be presented by the estimation of the rate constants of Reactions 3 and 11. The adopted rate constant[13] was $k_{-3}=k_{-11}(\mathrm{cm^3\ mol^{-1}\ s^{-1}})=2\times10^{13}$. The approximate rate constant of the forward Reaction 3 was estimated to be[11]

$$k_3(\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 3.5\times10^{13}\exp(-47400/RT). \quad (13)$$

In the estimation of the equilibrium constant of Reaction 11, the heat of formation of 59.6 kcal/mol[14] is used for $C_2H_3$ radical, the enthalpy and entropy being the same as those evaluated by Benson.[15] The approximate rate constant of forward Reaction 11 is given by

$$k_{11}(\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 8\times10^{13}\exp(-56400/RT). \quad (14)$$

The estimated $k_{11}$ is about two and one order of magnitude smaller than $k_3$ at 1000 and 1600 K, respectively.

Reaction 11 is not likely to occur as the primary initiation step for the pyrolysis and hydrogenation of acetylene in the $C_2H_2$–$H_2(D_2)$ system.

As regards the role of $C_4H_3$ radical and H atom in the pyrolysis, previously we could not determine the relative importance of $C_4H_3$ radical and H atom, since the kinetic behavior of the propagation steps initiated by $C_4H_3$ radical and H atom was expected to be similar, but we have obtained more data which may be useful to determine the relative importance of the above two radicals in the pyrolysis of acetylene.

Although the total yield of 1-buten-3-yne was little affected by the addition of deuterium, appreciable amounts of deuterated 1-buten-3-ynes were produced in the $C_2H_2$–$D_2$ system. Thus the isotopic distribution of 1-buten-3-yne together with those of ethylene and acetylene could be utilized for testing formation reactions of deuterated 1-buten-3-ynes, especially 1-buten-3-yne-$d_1$, the most abundant species among the deuterated isomers. The formation of 1-buten-3-yne and ethylene isomers in the $C_2H_2$–$D_2$ system seems complicated, a schematic reaction diagram being shown in Fig. 7.

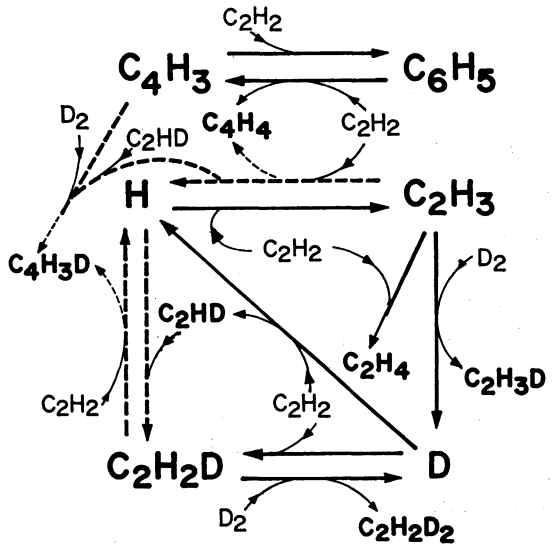


Fig. 7. Schematic reaction diagram for the major product formation in the $C_2H_2$–$D_2$ system. Solid line represents the reaction which is responsible for the formation of the relevant product, and broken line denotes ineffective reaction.

First the chain propagation step initiated by H atom, Reactions 4 and 5, will be considered. A considerable amount of $C_2HD$ is produced, which may result from the H–D exchange reaction between $C_2H_2$ and $D_2$ (Table 1). The $C_2HD$ in a considerable amount as well as $C_2H_2$ might participate in the formation of 1-buten-3-yne-$d_1$. If $C_4H_3D$ were mainly formed by the reaction of $C_2HD$ with the radicals, as an example, with $C_2H_3$ radical;

$$C_2H_3 + C_2HD \longrightarrow C_4H_3D + H, \quad (15)$$

the ratio of $[C_4H_3D]/[C_4H_4]$ would be given by

$$[C_4H_3D]/[C_4H_4] = (k_{15}/k_5)([C_2HD]/[C_2H_2]). \quad (16)$$

Since $k_5$ and $k_{15}$ (kinetic isotope effect) are expected to be approximately equal at high temperatures, the ratios of $[C_4H_3D]/[C_4H_4]$ and $[C_2HD]/[C_2H_2]$ as a function of temperature should be nearly same. However, this is not the case. Thus the paths of this type to form deuterated 1-buten-3-ynes are insignificant.

In the $C_2H_2$–$D_2$ system, $C_2H_3D$, instead of $C_2H_4$, is formed by the following reaction:

$$C_2H_3 + D_2 \longrightarrow C_2H_3D + D. \quad (17)$$

In order to be compatible with the observed isotopic distribution of ethylene, the D atom thus generated is quickly converted into H atom by

$$C_2H_2 + D \longrightarrow C_2HD + H. \quad (18)$$

Simultaneously a reaction analogous to Reaction 4 would occur as follows:

$$C_2H_2 + D \longrightarrow C_2H_2D. \quad (19)$$

The concentration of the $C_2H_3$ radical present in the system should be greater than that of the $C_2H_2D$ radical, since $C_2H_3D$ is the predominant species among the ethylene isomers. $C_2H_2D$ radical reacts with $D_2$ in a similar way:

$$C_2H_2D + D_2 \longrightarrow C_2H_2D_2 + D. \quad (20)$$

Reactions 17 and 20 are competitive with each other, the relative abundance of $C_2H_3D$ and $C_2H_2D_2$ being given by

$$[C_2H_2D_2]/[C_2H_3D] = (k_{20}/k_{17})([C_2H_2D]/[C_2H_3]). \quad (21)$$

On the other hand, the $C_2H_2D$ radical present in the system could lead to the formation of $C_4H_3D$ by a reaction with $C_2H_2$ analogous to Reaction 5:

$$C_2H_2D + C_2H_2 \longrightarrow C_4H_3D + H. \quad (22)$$

Similarly, the ratio of $[C_4H_3D]/[C_4H_4]$ is givn by

$$[C_4H_3D]/[C_4H_4] = (k_{22}/k_5)([C_2H_2D]/[C_2H_3]). \quad (23)$$

As in Eq. 16, $k_{17}=k_{20}$ and $k_5=k_{22}$ can be expected at the present temperatures. Then Eqs. 21 and 22 show that the relative abundance of $C_4H_3D$ and $C_4H_4$ would be comparable with that of $C_2H_2D_2$ and $C_2H_3D$. The observed ratios of $[C_4H_3D]/[C_4H_4]$ and $[C_2H_2D_2]/[C_2H_3D]$ as a function of temperature are summarized in Table 3. The above two ratios as a function of temperature differ from each other. Thus H atom may be an insignificant radical in the pyrolysis, but is primarily responsible for the formation of ethylene. It is concluded that $C_4H_3$ radical plays an important role in the formation of 1-buten-3-yne.

Table 3. Observed ratios of $[C_4H_3D]/[C_4H_4]$ and $[C_2H_2D_2]/[C_2H_3D]$ as a function of temperature

| | | | | | |
|---|---|---|---|---|---|
| $T_5$/K[a] | 1205 | 1245 | 1296 | 1371 | |
| $[C_4H_3D]/[C_4H_4]$[b] | —[c] | 0.006 | 0.058 | 0.354 | |
| $T_5$/K[a] | 1271 | 1313 | 1388 | 1407 | 1480 |
| $[C_2H_2D_2]/[C_2H_3D]$[b] | 0.171 | 0.176 | 0.258 | 0.266 | 0.538 |

a) $T_5$ is the temperature behind the reflected shock wave. b) The values are calculated from Tables 1 and 2 for the case of the mixture of $C_2H_2/D_2/Ar$= 10/10/80. c) Value not determined.

$C_4H_3D$ could not be formed by the reaction of $C_4H_3$ radical with $D_2$, since the concentration of $C_4H_3$ radical is a function of acetylene alone, and about half the

amount of $C_4H_3D$ produced in the mixture of $C_2H_2/D_2/Ar=10/10/80$ at around 1300 K could have been detected in the mixture of $C_2H_2/D_2/Ar=10/5/85$.

The ineffectiveness of the reaction of $C_4H_3$ radical with $H_2(D_2)$ may be understood in view of the heat of the reaction:[16]

$$C_4H_3 + H_2 \longrightarrow C_4H_4 + H, \quad \Delta H^\circ = 24.9. \quad (24)$$

The heat is greater than the activation energy of Reaction 7, which was estimated to be 17.9—22.6 kcal/mol.[11] The chain propagation process of Reactions 6 and 7 is more effective for the formation of 1-buten-3-yne than Reaction 24.

The occurrence of ethylene in a considerable amount is also in accordance with the prediction from the viewpoint of

$$C_2H_3 + H_2 \longrightarrow C_2H_4 + H, \quad \Delta H^\circ = 5.0. \quad (8)$$

The formation of $C_2H_4$ in a considerable amount in the $C_2H_2$–$D_2$ system cannot be accounted for by the reactions of the vinyl radicals with $D_2$. $C_2H_4$ thus can be formed by the hydrogen atom abstraction reaction of $C_2H_3$ radical from $C_2H_2$ molecule in the same way as in the pyrolysis of acetylene alone:

$$C_2H_3 + C_2H_2 \longrightarrow C_2H_4 + C_2H, \quad \Delta H^\circ = 12.7. \quad (25)$$

In a previous work the main primary $C_4$ product in the early stage of the pyrolysis of acetylene was concluded to be 1-buten-3-yne. If 1,3-butadiyne were formed at first and then reacted with $D_2$ to produce 1-buten-3-yne behind reflected shock wave and/or in the cooling process[17]

$$C_4H_2 + D_2 \longrightarrow C_4H_2D_2, \quad (26)$$

a significant amount of $C_4H_2D_2$ would be generated. This is inconsistent with the present isotopic distribution of 1-buten-3-yne.

*Formation Reaction for the Minor Products.* The secondary products of the pyrolysis were considerably affected by the addition of deuterium. The dependence of their yields on the deuterium concentration suggests that the minor products are produced by the reactions of the relevant radicals in the pyrolysis of acetylene by itself with deuterium.

In the present analysis, however, only the total yield of each minor product is obtained, and the $C_2H_2$–$H_2$ system will be considered in the following discussion. In the $C_2H_2$–Ar system the formation of $CH_4$ and $C_3H_4$ was interpreted in terms of the reactions of $CH_3$ and $C_3H_3$ radicals with acetylene molecule, respectively. In the $C_2H_2$–$H_2$ system, however, the radicals would react with $H_2$ rather than $C_2H_2$ molecule. In the case of the $CH_4$ formation the following two reactions would be competitive:

$$CH_3 + H_2 \longrightarrow CH_4 + H \quad \Delta H^\circ = -0.6, \quad (27)$$

$$CH_3 + C_2H_2 \longrightarrow CH_4 + C_2H \quad \Delta H^\circ = 7.1. \quad (28)$$

The heat of Reaction 27 is *ca.* 8 kcal/mol lower than that of Reaction 28. Reaction 27 is expected to have lower activation energy than that of Reaction 28.

A remarkable increase in the 1,3-butadiene yield in the $C_2H_2$–$H_2$ system can be ascribed to the reaction of $C_4H_5$ radical with hydrogen in a similar way:

$$C_2H_3 + C_2H_2 \longrightarrow C_4H_5, \quad \Delta H^\circ = -18.7, \quad (29)$$

$$C_4H_5 + H_2 \longrightarrow C_4H_6 + H, \quad \Delta H^\circ = 11.0. \quad (30)$$

All the minor products observed in the $C_2H_2$–$H_2$ system were also found in the pyrolysis of acetylene by itself at temperatures above 1300 K. On the other hand, in the presence of hydrogen (deuterium) they were produced at temperatures above 1100 K. This may be accounted for by the reactions stated above. Thus the addition of hydrogen to acetylene system appreciably increases the consumption of acetylene.

*Rate of Ethylene Formation.* The H atom generated by the initiation step is responsible for the formation of ethylene. The kinetic isotope effect is neglected and the $C_2H_2$–$H_2$ system is considered, since the total yield of ethylene was obtained for all runs. The rate of ethylene formation will be derived from the proposed mechanism.

In our mechanism the steady-state treatment is applicable in the same way as in the 1-buten-3-yne formation.[11] The recombination reaction of H atom with $C_2H_3$ radical is not important, since $C_2H_3$ radical is predominant. Neglecting the backward reactions, the steady-state assumption is applied to the scheme of Reactions 3, 4, 8, and 9. The steady-state rate of the ethylene formation is given by

$$d[C_2H_4]/dt = k_8(k_3/2k_9)^{1/2}[C_2H_2][H_2]. \quad (31)$$

$k_8$ is calculated from $k_{-8}$ evaluated by Schofield[18] by the combination of the equilibrium constant of Reaction 8 at 1300 K, and $k_9$ is taken equal to $k_t$ in Ref. 11:

$$k_8(\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 5.39\times10^{11}\exp(-12900/RT), \quad (32)$$

$$k_9(\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 2.9\times10^{12}. \quad (33)$$

Substituting these values in Eq. 30, the second-order rate constant is given by

$$k_8(k_3/2k_9)^{1/2}(\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 1.6\times10^{12}\exp(-36600/RT). \quad (34)$$

The steady-state rate constant agrees with the observed (Eq. 2) within a factor of 2 in the temperature range studied.

When a large excess of hydrogen present relative to acetylene, the initiation step of Reaction 11 may become more important. Taylor and Van Hook[1] reported the higher activation energy of 42 kcal/mol for the mixtures of $C_2H_2/H_2=1$—$1/32$ in the temperature range 770—810 K. This might be related to the change of the initiation step from Reaction 3 to 11, the activation energy of which is estimated to be higher than that of Reaction 3.

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