Pyrolysis of Acetylene behind Shock Waves

Hiroo Ogura

Institute of Space and Aeronautical Science, The University of Tokyo,
Komaba, Meguro-ku, Tokyo 153

(Received November 12, 1976)

The pyrolysis of acetylene was investigated behind the reflected shock waves in a single-pulse shock tube over the temperature range from 1000 to 1670 K. The major products were 1-buten-3-yne, 1,3-butadiyne, and hydrogen. The main primary C_4 product, however, changes from 1-buten-3-yne to 1,3-butadiyne with the increase of temperature. At the lower temperatures the formation of 1-buten-3-yne dominates the pyrolysis of acetylene. The rate of 1-buten-3-yne formation is second order with respect to acetylene concentration, and its second-order rate constant is expressed as follows:

$$k(\mathrm{cm^3\,mol^{-1}\,s^{-1}})=10^{14.39\pm0.26}\exp((-46400\pm1400)/RT)$$

The isotopic distribution of 1-buten-3-yne in the pyrolysis of the equimolar C_2H_2 and C_2D_2 mixture, proved that the pyrolysis proceeds *via* a free-radical mechanism. A free-radical chain mechanism initiated by the bimolecular reaction of acetylene, $2C_2H_2 \rightarrow C_4H_3 + H$, was proposed.

The thermal decomposition of acetylene has been studied over a wide temperature range by various methods. At low and intermediate temperatures, static[1–6] and flow[7–16] systems were employed and the reaction rate of acetylene consumption, reaction order, products distribution, wall effects, and the effects of a variety of additives, for example, reaction products and radical scavengers such as nitrogen oxide, were extensively investigated.

There is substantial agreement on some aspects of the pyrolysis at low and intermediate temperatures. At the initial stage of the reaction, an induction period is observed and succeeded by a homogeneous reaction. The latter is second order with respect to acetylene with a low activation energy of 40—50 kcal*/mol. The reaction leads to the formation of high molecular weight compounds and is inhibited markedly by nitric oxide. The polymer produced at the early stage is solely 1-buten-3-yne(vinylacetylene), and benzene is an important secondary product. Palmer and Dormish[15] have shown that there is a transition as regards the primary C_4 product at about 1500 K, where 1,3-butadiyne (diacetylene) becomes predominant.

In high temperature region shock tube technique was used exclusively, because it is excellent to realize high temperature without worry about wall effects. The experimetal results obtained from the shock tube studies,[17–28] however, are somewhat confusing with regard to the reaction order and the main C_4 product, butenyne or butadiyne. These discrepancies may be ascribed to the difficulties to analyze the reaction products and to determine the reaction order by shock tube technique. It seems desirable to study the pyrolysis over a fairly wide temperature range, the lower of which overlaps the flow tube investigations.

The mechanism of the pyrolysis has not been well established. Many investigators favored a bimolecular reaction of acetylene to give an excited molecule of acetylene or butenyne in the triplet state or biradical. Recently several attempts have been made to interpret the pyrolysis of unsaturated hydrocarbons in terms of free-radical chain mechanisms initiated by the bimolecular reactions of unsaturated hydrocarbons,[29,30] and have attracted the attention of many investigators. In the shock tube experiments above 1700 K, Gay and coworkers,[25] and Bopp and Kern[28] detected C_4H_3 radical by use of a time of flight mass spectrometer.

In the present experiment, a wide temperature range from 1000 to 1670 K was covered. Complete analysis of the reaction products was performed as far as possible. Particular attention has been paid to determine the order of the reaction and the major products as a function of temperature. In the temperature range studied, it is difficult to find radicals in a direct manner,[12] but the deuterium content of the main primary product in the pyrolysis of the equimolar C_2H_2 and C_2D_2 mixture, may be expected to provide information for testing the mechanisms.

Experimental

Apparatus and Procedure. The pyrolysis was studied in a 4-cm i.d. single-pulse shock tube. The driven section was 277 cm long, the main portion of which was made of terex glass tubing. The driver section was steel tubing and its length was variable, but it was fixed at 157 cm in the present runs. A 80-l dump tank was connected to the driven section near the diaphragm. The driver section was seperated from the driven section by a "Lumirror" (polyethylene terephthalate) film of 0.05 mm thickness. The details of the shock tube was described by Tsuda and Kuratani,[31] but a slight modification was made.

Before each test run, the shock tube was evacuated to below 1×10^{-4} Torr by an oil diffusion pump. The ultimate vacuum was 8×10^{-5} Torr, and the leak plus outgassing rate was approximately 6×10^{-5} Torr/min.

In order to measure the incident shock velocity, the outputs of the three pressure gauges(barium titanate-lead zirconate) spaced at 23.1 cm intervals were fed into a home-built electronic counter(Hop Step Jump Counter),[32] having the accuracy of 0.1 μs. Reflected shock parameters were calculated from the incident shock velocity extrapolated to the end-plate, considering the attenuation of the shock wave. Ideal shock wave theory was used. The thermodynamical data were taken from the JANAF tables.[33] The pressure profiles at the downstream end were recorded on an oscilloscope, from which the reaction times were determined with the accuracy of ±5%. Helium was used as the driver gas throughout the experiment. The shocks were fired within five minutes after the two section were filled with the desired gases.

---

[*] 1 $\mathrm{cal_{th}}=4.184$ J.

Materials. The three kinds of mixtures, with the ratios of C_2H_2/Ar equal to 5/95 and 10/90; and with the ratio of C_2H_2/C_2D_2/Ar equal to 5/5/90, were prepared in a glass vessel of 5-1 volume, and were allowed to stand at least one day before use.

Acetylene, from Matheson Company, was bubbled through concentrated sulfuric acid, passed through a sodalime tower and then collected in a liquid nitrogen trap. The condensate was purified by bulb-to-bulb vacuum distillation. Acetylene-d_2(99% D atom guaranteed) was obtained from Merck Sharp and Dohme of Canada. For the purification, it was condensed in a liquid nitrogen trap, and subjected to a brief pumping period. Argon(nominal purity of 99.9995%), from Nippon Sanso Co., was used without further purification and served as the diluent.

Butenyne and butadiyne were prepared from 1,3-dichloro-2-butene and 1,4-dichloro-2-butyne, respectively.[34,35] They were purified by distillation through a low temperature column. The purified gases were quickly diluted with a large amount of argon as the stabilizer, and stored. Gas chromatographic analysis showed that the butenyne and butadiyne contained allene, propyne, and butadiene as the impurities. The purity of the butenyne and butadiyne was found 82.0 and 91.4%, respectively.

Research Grade CH_4, C_2H_4, C_2H_6, allene, propyne, and 1,3-butadiene were obtained from Takachiho Shoji Co., and used as received. The reference gases for the gas chromatographic calibration were prepared barometrically with mercury and oil manometers. Argon was used as the diluent gas.

Analytical. As soon as the shock was fired, the test gas around the end-plate was quickly extracted into an evacuated bulb of 60-ml volume with the aid of a solenoid valve operated by compressed air. The hydrocarbons in the products were analyzed on Yanaco G-80 and Shimadzu GC-3AF gas chromatographs using flame ionization detectors. CH_4, C_2H_4, C_2H_6 were analyzed at 50 °C on a 3 mm × 2 m column packed with 80—100 mesh Porapak N. The higher molecular weight hydrocarbons were analyzed at 130 °C. The hydrogen was detected at a room temperature by a thermal conductivity cell, on a 4-m column packed with 40—50 mesh molecular sieve 5A with argon as the carrier gas. The concentration of each product was determined from the peak area relative to that of the reference gas.

The shock heated samples of the equimolar mixture of C_2H_2 and C_2D_2 in argon were analyzed by a Hitachi model RM-50 mass spectrometer to determine the isotopic distributions of acetylene and butenyne. The ionization potential was kept at 50 eV. The pattern coefficient of acetylene-d_1 was taken equal to the arithmetical mean of those acetylene-d_0 and acetylene-d_2. The fragmentation patterns of butenyne isomers were calculated statistically from that of butenyne-d_0 assuming the same fragmentation.

Results

The two mixtures with the ratios of C_2H_2/Ar equal to 5/95 and 10/90 were pyrolyzed over the temperature range from 1000 to 1670 K. The shock heated samples were analyzed by gas chromatography. Complete analysis was carried out for the hydrocarbons having carbon number from 1 to 4.

Major Products. Under the experimental conditions employed, the major products of the pyrolysis were butenyne, butadiyne, and hydrogen. Butenyne and butadiyne were identified by both gas chromatography and mass spectrometry. The analytical results are shown in Fig. 1. As shown in Fig. 1, at the lower temperatures the yield of butenyne increases with temperature. And it attains to its maximum at about 1500 K, and then with the increase of temperature, it becomes to decrease.

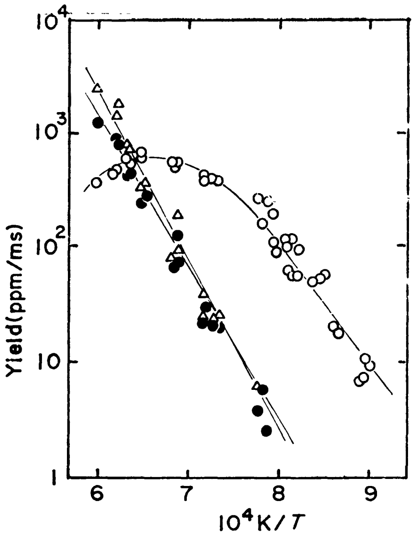

Fig. 1. Major products distribution as a function of temperature. (C_2H_2/Ar=5/95).
○: Butenyne, ●; butadiyne, △; hydrogen.

The yields of butadiyne and hydrogen increase linearly with increasing temperature in the temperature range studied. At the lower temperatures approximately equal amounts of butadiyne and hydrogen are produced, while at the higher temperatures above 1500 K the yield of hydrogen evidently goes beyond that of batadiyne. It is thus confirmed that at the lower temperatures butenyne is the main primary product, on the other hand, butadiyne and hydrogen become predominant at the higher temperatures.

Minor Products. CH_4, C_2H_4, allene, and propyne were found as the minor products. They are shown in Fig. 2 in the case of the mixture of C_2H_2/Ar=10/90. On the gas chromatograph a low and broad peak with a very long retention time (about 3 h) was observed, and identified as benzene. But the quantitative analysis was not carried out. In addition, trace amounts(less than 1 ppm) of C_2H_6 and 1,3-butadiene were detected. It is noteworthy that the hydrocarbons containing odd number of carbon atoms such as CH_4 and C_3H_4 were observed.

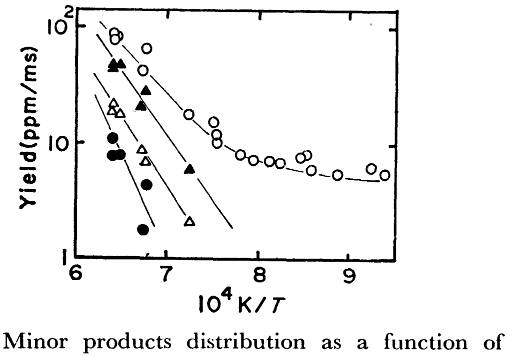

Fig. 2. Minor products distribution as a function of temperature. (C_2H_2/Ar=10/90)
○; Ehtylene, △; allene, ▲; propyne,
●; methane.

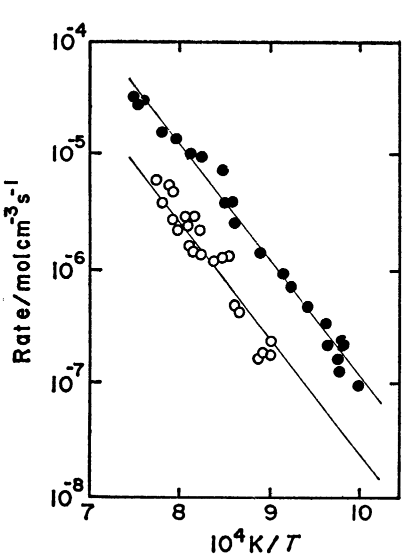

Fig. 3. Dependence of the rate of butenyne formation on acetylene concentration.
○; C_2H_2/Ar=5/95, ●; C_2H_2/Ar=10/90.

Formation Rate of Butenyne. The two kinds of mixtures stated above also served to determine an empirical reaction rate formula of butenyne formation. The total densities behind the reflected shock waves were $(2.35\pm0.11)\times10^{-5}$ mol/cm^3 throughout all runs. And the reaction times were limited within 1 ms to maintain the low conversions of acetylene. Since we are concerned with the early stage of the pyrolysis, where the yields of butadiyne and hydrogen are negligible compared with that of butenyne, only the data obtained below 1350 K are collected. The dependence of the rate of butenyne production on the acetylene concentration is shown in Fig. 3. The empirical power rate equation such as, $d[C_4H_4]/dt=A\exp(-E/RT)[C_2H_2]^n$, was assumed. Applying the method of least squares to A, E, and n;

$$d[C_4H_4]/dt = k_1[C_2H_2]^{2.35\pm0.15} \tag{1}$$

where

$$k_1 = 10^{16.74\pm1.05}\exp((-48000\pm1500)/RT) \tag{2}$$

was obtained in cm^3 mol^{-1} s^{-1} units. The errors denote the standard deviation of the least squares method.

In the literatures of the shock tube studies, first[19,24,26] or second[20-23,25] order rate with respect to acetylene was reported. And in the context of the first or second order reaction, the second-order reaction is supported from the present analysis. Therefore, when we take the view of the second-order reaction, the experimental data will be fitted by the following rate constant:

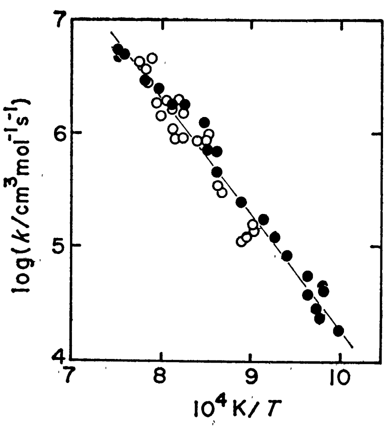

Fig. 4. Arrhenius plot of the second-order rate constants.
○; C_2H_2/Ar=5/95, ●; C_2H_2/Ar=10/90.

$$k_3(\text{cm}^3\,\text{mol}^{-1}\,\text{s}^{-1}) = 10^{14.39\pm0.26}\exp((-46400\pm1400)/RT) \tag{3}$$

The Arrhenius plot of the second-order rate constant is shown in Fig. 4.

Isotopic Distribution. The equimolar mixture of C_2H_2 and C_2H_2 in argon was shock heated below 1350 K, and the isotopic distributions of butenyne and acetylene were determined by mass spectrometry. In the temperature range up to 1350 K, the interference due to butadiyne on the mass spectra of butenyne isomers could be neglected, for the amount of butadiyne formed was negligibly small compared with that of butenyne. The results of the mass spectral analyses are given in Table 1. Evidently, considerable amounts of butenyne isomers containing odd number of hydrogen and deuterium atoms, C_4H_3D and C_4HD_3, are produced. This finding may be useful for testing the proposed mechanisms, which will be discussed in the following section.

Discussion

Comparison of the Second-order Rate. An exact analysis showed that at the early stage of the pyrolysis, butenyne is the main primary product, and the second-order rate with respect to acetylene is preferred for the formation of butenyne. It is noticed that the second-order rate constants for the consumption of acetylene

Table 1. Isotopic distribution of butenyne

T_5 [a) / K	C_4H_4 [b)	C_4H_3D	$C_4H_2D_2$	C_4HD_3	C_4D_4	C_2HD [b)	τ [c) / μs
1069	0.159	0.155	0.262	0.280	0.143	0.005	790
1180	0.161	0.167	0.304	0.261	0.107	0.011	860
1185	0.171	0.169	0.303	0.248	0.108	0.012	760
1201	0.152	0.176	0.306	0.256	0.110	0.013	700
1285	0.147	0.190	0.320	0.237	0.106	0.024	870
1325	0.148	0.189	0.324	0.249	0.090	0.075	880

a) T_5 is the temperature behind the reflected shock wave. b) The total amounts of butenyne and acetylene are taken equal to 1.000, respectively. c) τ is the dwell time.

obtained by many investigators, covering the temperature range 620—2450 K, apparently lie on a single Arrhenius expression:[25)]

$$k_4(\mathrm{cm^3\,mol^{-1}\,s^{-1}}) = 10^{13.8}\exp(-41600/RT) \qquad (4)$$

At the early stage of the pyrolysis, the relationship of $2d[C_4H_4]/dt = -d[C_2H_2]/dt$ holds well, since butenyne is the only reaction product and the other minor products may be neglected. In the temperature range 1000—1350 K the absolute values of $2k_3$ agree well with those of k_4.

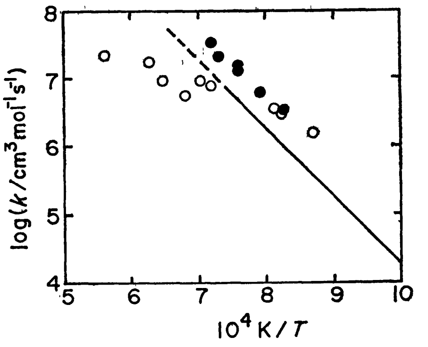

Fig. 5. Comparison of the second-order rate constant of butenyne formation with the literatures.
○; Skinner and Sokoloski, ●; Towell and Martin, ——; this work.

The second-order rate constants for butenyne formation were obtained by only two groups; by Towell and Martin in a flow tube study[14)] and by Skinner and Sokoloski in a shock tube experiment.[20)] A comparison with the literatures is made in Fig. 5. The absolute values of the present rate constant are about a factor of 0.5 lower than those obtained by them in the temperature range 1000—1350 K. But when the activation energy is compared, the present rate constant is in good agreement with that of Towell and Martin's rather than with that of Skinner and Sokoloski's. The rate constant derived by Towell and Martin is expressed as:

$$k_5(\mathrm{cm^3\,mol^{-1}\,s^{-1}}) = 10^{14.5}\exp(-45000/RT) \qquad (5)$$

As shown in Fig. 1, the concentration of butenyne has a maximum value. Consequenly, in the neighborhood of the temperature where the yield of butenyne shows its maximum, the increase of butenyne concentration slows down with increasing temperature. It seems probable that under the conditions employed by Skinner and Sokoloski, the apparent lower activation energy may be obtained by the reason mentioned above.

As far as the second-order rate is concerned, the absolute values are fairly well consistent among many investigators, although there are significant dissents as to the main primary product of the pyrolysis.

The reaction products observed in the present analysis, are in good accordance with those detected in static and flow systems, for example, Cullis and Franklin[16)] reported butenyne, butadiyne, CH_4, C_2H_4, C_2H_6, H_2, propyne, and benzene as the reaction products. Further, the nature and sequence of the formation of their products as a function of time have strong resemblance to those in the present shock tube experiment as a function of temperature. This may suggest that the same or similar mechanism is operative in the temperature range up to 1350 K, where the formation of butenyne is predominant.

Mechanism of Butenyne Formation. The strong inhibition by nitric oxide observed especially at low temperatures[2,3,5)] cannot be accounted for by a simple bimolecular reaction of acetylene. The excited-state molecule mechanisms were proposed to be compatible with the low activation energy and the inhibition by radical scavengers. The following molecular chain mechanism involving excited-state molecules was presented as the most probable one to explain the fairly high frequency factor;[2,15)]

$$C_2H_2 + C_2H_2 \rightarrow C_2H_2{}^* + C_2H_2 \qquad \text{initiation}$$

$$\left.\begin{array}{l} C_2H_2{}^* + C_2H_2 \rightarrow C_4H_4{}^* \\ C_4H_4{}^* + C_2H_2 \rightarrow C_4H_4 + C_2H_2{}^* \end{array}\right\} \text{chain propagation}$$

where, $C_2H_2{}^*$ and $C_4H_4{}^*$ were supposed to be the excited molecules in the triplet state or biradicals.

In the pyrolysis of the equimolar mixture of C_2H_2 and C_2D_2, C_4H_3D and C_4HD_3 would be formed by the reaction of C_2HD molecule with C_2H_2 and C_2D_2 molecules, respectively. C_2HD molecule may result from the H–D exchange reaction between C_2H_2 and C_2D_2 molecules.

As can be seen from Table 1, the yields of C_4H_3D and C_4HD_3 are too large to be accounted for by the above mechanism, because the yield of C_2HD in the present experiment is less than 10% of the initial acetylene concentration.

The appearance of C_4H_3D and C_4HD_3 in significant quantities in the C_2H_2–C_2D_2 system may suggest that the pyrolysis of acetylene proceeds *via* a free-radical mechanism. The acitivation energy of 46.4 kcal/mol is too low to allow the initiation process of unimolecular scission of bonds, C≡C and C–H, in acetylene molecule. We have tried to interpret our data in terms of a free-radical chain mechanism initiated by a bimolecular reaction of acetylene. This attempt is basically an extention of that proposed by Back.[36)] And in this study each reaction participated in the pyrolysis was examined in detail from the thermochemical point of view.

The heats of formation for the relevant C_4 molecules and radicals used in the following calculation are the same as those evaluated by Cowperwaite and Bauer,[37)] and the heat of formation of 59.6 kcal/mol, the smallest value in the literatures, is adopted for C_2H_3 radical.[38)] The other values are taken from the JANAF tables. The standard heats of the reactions, ΔH°(kcal/mol), are given at 298 K.

The most probable free-radical chain mechanism is represented as follows:

$$2C_2H_2 \rightarrow C_4H_3 + H \qquad \Delta H^\circ = 46.2 \qquad (6)$$

$$H + C_2H_2 \rightarrow C_2H_3 \qquad \Delta H^\circ = -46.7 \qquad (7)$$

$$C_2H_3 + C_2H_2 \rightarrow C_4H_4 + H \qquad \Delta H^\circ = 13.6 \qquad (8)$$

$$C_4H_3 + C_2H_2 \rightarrow C_6H_5{}^{39)} \qquad \Delta H^\circ \simeq -22.0 \qquad (9)$$

$$C_6H_5 + C_2H_2 \rightarrow C_4H_4 + C_4H_3 \qquad \Delta H^\circ \simeq -11.0 \qquad (10)$$

Ethynylvinyl(C_4H_3) radical has two isomers, 1-ethynylvinyl and 2-ethynylvinyl radicals. The heat of formation of the former radical is about 20 kcal/mol lower than that of the latter.[40] In our mechanism C_4H_3 is supposed to be 1-ethynylvinyl radical, since it is more advantageous than 2-ethynylvinyl radical in the view of the enthalpy change of Reaction 6.

In the above mechanism Reactions 8 and 10 are regarded as elementary reactions. In reality, however, the formation of C_4H_4 proceeds *via* relevant hot radical, for example, $C_4H_5^*$ in the case of Reaction 8. And when the energy present in the hot radical $C_4H_5^*$ is low enough, the hot radical may be stabilized by the collision with the third body to the C_4H_5 radical. Thus Reaction 8 should be divided into the following two reactios;

$$C_2H_3 + C_2H_2 \rightarrow C_4H_5 \qquad \Delta H^\circ = -33.4 \quad (11)$$

$$C_4H_5 \rightarrow C_4H_4 + H \qquad \Delta H^\circ = 47.0 \quad (12)$$

Reactions 11 and 12 show that C_4H_4 is formed by addition and subsequent decomposition reactions of the radicals. For simplicity the reactions of both types will be referred to addition-decomposition reactions hereafter.

The chain propagation processes to form butenyne are composed of addition reaction to acetylene and subsequent addition-decomposition reaction. Both radicals, C_4H_3 and H, generated by the initiation step can lead to the production of butenyne .

When the equimolar mixture of C_2H_2 and C_2D_2 in argon is pyrolyzed, appreciable amounts of C_4H_3D and C_4HD_3 among the butenyne isomers will be produced by the above mechanism. This prediction is consistent with the observed isotopic distribution of butenyne summarized in Table 1.

The isotopic distribution for the above mechanism was calculated in the case where H atom and C_2H_3 radical are predominant. If equal collision probability for C_2H_2 and C_2D_2 is assumed and the kinetic isotope effect is neglected, H and D atoms are produced by Reaction 6 in equal amounts, and the amounts of vinyl radical isomers, C_2H_3, C_2H_2D, C_2HD_2, and C_2D_3 formed by Reaction 7 are also equal. And then C_2H_2D radical, for instance, will react with C_2D_2 in the following process:

$$\begin{aligned} \mathrm{HDC{=}\dot{C}H} + \mathrm{DC{\equiv}CD} &\rightarrow \mathrm{HDC{=}CHCD{=}\dot{C}D} \\ &\rightarrow \mathrm{HDC{=}CHC{\equiv}CD}(C_4H_2D_2) + \mathrm{D} \end{aligned} \qquad (13)$$

By the similar reactions to Reaction 13, the equal amounts of H and D atoms will be generated again. The above estimation produces the ratios among the butenyne isomers, $C_4H_4/C_4H_3D/C_4H_2D_2/C_4HD_3/C_4D_4 = 1/2/2/2/1$. The agreement between the calculated and the observed values seems considerably good. The similar isotopic distribution of butenyne may be obatined when the chain propagation step of Reactions 9 and 10 is dominant.

In order to estimate the rate constant of the initiation step of Reaction 6, the enthalpy and entropy of C_4H_3 radical were calculated from the spectroscopic data of butenyne[41] following the evaluation method presented by O'Neal and Benson.[42] At 1300 K the enthalpy and entropy changes of Reaction 6 are 47.4 kcal/mol and 1.16 cal K^{-1} mol,$^{-1}$ respectively. The reverse rate constant of Reaction 6 is uncertain, but may be assumed to be the same as that of recombination reaction of atom with radical estimated by Benson and O'Neal:[43]

$$k_{-6}(\mathrm{cm^3\,mol^{-1}\,s^{-1}}) = 10^{13.3} \qquad (14)$$

Then combining Eq. 14 with the equilibrium constant at 1300 K, the approximate forward reaction rate constant is given by:

$$k_6(\mathrm{cm^3\,mol^{-1}\,s^{-1}}) = 10^{13.55}\exp(-47400/RT) \qquad (15)$$

An alternative initiation step was proposed by Back:[36]

$$2C_2H_2 \rightarrow C_2H + C_2H_3 \qquad \Delta H^\circ = 65.2 \qquad (16)$$

And the estimated rate constant was given by:

$$k_{16}(\mathrm{cm^3\,mol^{-1}\,s^{-1}}) = 10^{15.7}\exp(-70000/RT) \qquad (17)$$

The frequency factor of k_{16} seems abnormally high,[44] and k_6 is above ten times faster than k_{16} in the temperature range 1000—1350 K. Therefore, it may be concluded that Reaction 16 is not likely to occur as the initiation step for the formation of butenyne. Reaction 16, however, may be more important at higher temperatures than Reaction 6 in the view of the entropy change.[28]

In the above mechanism the termination occurs *via* the recombination or disproportionation reaction of the radicals involved. For the rate constants of the termination, the recombination rate constant of alkyl radical with radical[43] may be used as an alternative one;

$$k_t(\mathrm{cm^3\,mol^{-1}\,s^{-1}}) = 10^{12.3} \qquad (18)$$

where, k_t is rate constant of the termination reaction.

Under the present shock tube experiment the reaction times are extremely short. This provides a serious problem in applying the steady-state assumption to the system stated above. As to the formation of butenyne, however, Silcocks,[2] and Cullis and Franklin[16] observed no appreciable induction period at lower temperatures. Accordingly the assumption of steady-state of the radicals may apply to some extent. Imposing the steady-state of the radicals on the above mechanism, the second-order rate of butenyne formation is expressed as;

$$\mathrm{d}[C_4H_4]/\mathrm{d}t(\mathrm{mol\,cm^{-3}\,s^{-1}}) = k_{\mathrm{ad}}(k_6/2k_t)^{1/2}[C_2H_2]^2 \qquad (19)$$

where, k_{ad} is the rate constant of Reaction 8 or 10. By the comparison with the observed second-order rate constant k_3, k_{ad} in Eq. 19 is derived as follows:

$$k_{\mathrm{ad}}(\mathrm{cm^3\,mol^{-1}\,s^{-1}}) = 10^{13.9}\exp(-22600/RT) \qquad (20)$$

When compared with the rate constant $k_4/2$:

$$k_{\mathrm{ad}}(\mathrm{cm^3\,mol^{-1}\,s^{-1}}) = 10^{13.0}\exp(-17900/RT) \qquad (21)$$

The addition and addition-decomposition reactions may compete with each other. And the addition of the radicals to acetylene may proceed successively at the lower temperatures, since the addition reaction to acetylene has, in general, lower activation energy than that of the addition-decomposition reaction. Consequently butenyne may be produced by the subsequent addition-decomposition reaction. In the case of the competition between Reactions 8 and 11, butenyne may be formed by the reaction of C_4H_5 radical with acetylene:

$$C_4H_5 + C_2H_2 \rightarrow C_4H_4 + C_2H_3 \quad \Delta H° = 13.3 \quad (22)$$

Generally the bond dissociation energy of C–C is lower than that of C–H bond in the larger radicals, and low molecular weight molecules may be formed by the C–C bond scission rather than the C–H bond fission at the lower temperatures. In some experiments at the lower temperatures benzene is reported as the main primary product.[11,13] This might be interpreted in the similar way:

$$C_6H_5 + C_2H_2 \rightarrow C_8H_7 \quad (23)$$

$$C_8H_7 + C_2H_2 \rightarrow C_6H_6(\text{benzene}) + C_4H_3 \quad (24)$$

As mentioned above, the chain propagation steps consist of addition and addition-decomposition reactions, and both of which may be expected to show similar kinetic behavior regardless of different radicals involved. An Arrhenius plot linear within the error limits involved in the measurement of acetylene pyrolysis[25] is therefore consistent with our mechanism. Palmer and Dormish[15] pointed out that the Arrhenius plot of the data in the literatures shows a discontinuity in the neighborhood of 1000 K, and suggested a change of the mechanism of the pyrolysis. But on the basis of the similarities that exist between frequency factors and activation energies of homologous reactions, it seems more likely that from the kinetic data obtained at low temperatures where the formation of butenyne dominates, we can predict no change of the chain propagation step in the mechanism.

Furthermore, the chain propagation steps initiated by H atom and C_4H_3 radical, respectively, will show quite similar kinetic behavior. Thus in the present stage we could not determine the relative importance of H atom and C_4H_3 radical in the above mechanism. Further study as regards the relative importance of the two radicals, C_4H_3 and H, is in progress.

Formation of Butadiyne and Hydrogen. At the higher temperatures the formation of butadiyne and hydrogen becomes important, which may be interpreted in terms of a free-radical chain mechanism in the same way. The abstraction reaction of H atom from acetylene becomes faster than the addition of H atom to acetylene with increasing temperature. The following chain propagation may dominate:[28,34]

$$H + C_2H_2 \rightarrow H_2 + C_2H \quad \Delta H° = 7.7 \quad (25)$$

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H \quad \Delta H° = -4.8 \quad (26)$$

The alternative scheme of Reaction 26 is as follows:

$$HC{\equiv}C\cdot + HC{\equiv}CH \rightarrow HC{\equiv}CCH{=}\dot{C}H \quad \Delta H° = -44.8 \quad (27)$$

$$HC{\equiv}CCH{=}\dot{C}H \rightarrow HC{\equiv}C{-}C{\equiv}CH + H \quad \Delta H° = 40.0 \quad (28)$$

As shown in Reaction 27, the stabilized C_4H_3 radical is 2-ethynylvinyl radical, which is different from that produced by Reaction 6.

At the higher temperatures covered in the present experiment the amount of hydrogen is greater than that of butadiyne. This implies that another path to yield hydrogen is operative, since by the above chain propagation nearly equal amounts of hydrogen and butadiyne may be formed. One of the possible paths is the decomposition of butenyne by the following reactions:

$$H + C_4H_4 \rightarrow H_2 + C_4H_3 \quad \Delta H° = -24.9 \quad (29)$$

$$C_2H + C_4H_4 \rightarrow C_2H_2 + C_4H_3 \quad \Delta H° = -32.6 \quad (30)$$

In the present experiment the sum of carbon atom over the whole products was less than that of hydrogen atom. There must have been some undetected hydrocarbons present, containing on the average less than one atom of hydrogen per atom of carbon. Thus C_6H_2 and C_8H_2[25,26] appear possible hydrocarbons undetected in the present analysis. As the pyrolysis continues the following reactions may be expected to occur;

$$H + C_4H_2 \rightarrow C_4H + H_2 \quad (31)$$

$$C_4H + C_2H_2 \rightarrow C_6H_2 + H \quad (32)$$

and succeeded by:

$$H + C_6H_2 \rightarrow C_6H + H_2 \quad (33)$$

$$C_6H + C_2H_2 \rightarrow C_8H_2 + H \quad (34)$$

The formation of carbon soot becomes very important with increasing temperature at high temperatures. But this problem is beyond our discussion. Under the experimental conditions studied, however, the formation of soot was insignificant.

As shown in Fig. 1, the activation energies of butadiyne and hydrogen formation are higher than that of butenyne. Assuming the second-order rates for butadiyne and hydrogen production, the activation energies of 69.5 and 77.6 kcal/mol were obtained, respectively. If the formation of butadiyne and hydrogen were the predominant reaction consuming acetylene, the low activation energy of 41.6 kcal/mol of k_4 would be difficult to be accounted for. Therefore, the secondary reactions which consume acetylene, with lower activation energies than those of the main reactions, or which reproduce acetylene might contribute to lowering the apparent activation energy of the over-all acetylene consumption reaction.

Secondary Products. As the minor products the hydrocarbons containing odd number of carbon atoms, CH_4 and C_3H_4, were produced. The formation of these products may be easily accounted for by the reaction of the radical involved in the mechanism stated above. For example, CH_3 radical may be formed by the isomerization and decomposition of C_6H_7 radical as follows;[36]

$$C_4H_5 + C_2H_2 \rightarrow H_2C{=}CH{-}CH{=}CH{-}CH{=}\dot{C}H \quad (35)$$

and then 1,5 hydrogen shift may occur:

$$\rightarrow H_3C{-}\dot{C}H{-}CH{=}CH{-}C{\equiv}CH \quad (36)$$

The terminal methyl group may split off to CH_3 radical. CH_3 radical will abstract a hydrogen atom from acetylene to form CH_4 molecule. C_3H_3 radical may be generated in the similar way, which will ultimately lead to the formation of allene and propyne. Benzene may also be produced from C_6H_7 radical:[45]

$$C_6H_7 \rightarrow C_6H_6(\text{benzene}) + H \quad (37)$$

The formation of benzene provides an evidence that the chain of carbon atoms has extended to six within the reaction times in the present experiment. And the participation of C_6 radicals may be justified. Considerable amount of ethylene was obtained in the persent analysis. There are two possible paths to yield ethylene:

$$C_2H_3 + C_2H_2 \rightarrow C_2H_4 + C_2H \qquad \Delta H^\circ = 12.7 \qquad (38)$$

$$2C_2H_3 \rightarrow C_2H_4 + C_2H_2 \qquad \Delta H^\circ = -52.5 \qquad (39)$$

The trace amounts of ethane and 1,3-butadiene may result from the recombination reactions of two CH_3 and C_2H_3 radicals, respectively. The ratio of disproportionation reaction rate constant to that of recombination is uncertain, but it is more likely that ethylene is formed mainly by the reaction of C_2H_3 radical with acetylene.

The author would like to thank Professor Kenji Kuratani, The University of Tokyo, for his valuable discussions and suggestions throughout this investigation.

References

1) H. A. Taylor and A. Van Hook, *J. Phys. Chem.*, **39**, 811 (1935).

2) C. G. Silcocks, *Proc. R. Soc. London, Ser. A*, **242**, 411 (1957).

3) G. J. Minkoff, D. M. Newitt, and P. Rutledge, *J. Appl. Chem.*, **7**, 406 (1957).

4) G. J. Minkoff, *Can. J. Chem.*, **36**, 131 (1958).

5) C. F. Cullis, G. J. Minkoff, and M. A. Nettleton, *Trans. Faraday Soc.*, **58**, 1117 (1962).

6) C. F. Cullis and M. A. Nettleton, *Trans. Faraday Soc.*, **59**, 361 (1963).

7) R. N. Pease, *J. Am. Chem. Soc.*, **51**, 3470 (1929).

8) E. A. Westbrook, K. Hellwig, and R. C. Anderson, *Int. Symp. Combust.*, **5**, 631 (1955).

9) F. C. Stehling, J. D. Frazee, and R. C. Anderson, *Int. Symp. Combust.*, **6**, 247 (1957).

10) R. S. Slysh and C. R. Kinney, *J. Phys. Chem.*, **65**, 1044 (1961).

11) F. C. Stehling, J. D. Frazee, and R. C. Anderson, *Int. Symp. Combust.*, **8**, 775 (1962).

12) K. C. Hou and R. C. Anderson, *J. Phys. Chem.*, **67**, 1579 (1963).

13) M. S. B. Munson and R. C. Anderson, *J. Phys. Chem.*, **67**, 1582 (1963).

14) C. D. Towell and J. J. Martin, *AIChE J.*, **7**, 693 (1963).

15) H. B. Palmer and F. L. Dormish, *J. Phys. Chem.*, **68**, 1553 (1964).

16) C. F. Cullis and N. H. Franklin, *Proc. R. Soc. London, Ser. A*, **280**, 139 (1964).

17) C. F. Aten and E. F. Greene, *Discuss. Faraday Soc.*, **22**, 162 (1956).

18) E. F. Greene, R. L. Taylor, and W. L. Patterson Jr., *J. Phys. Chem.*, **62**, 238 (1958).

19) W. J. Hooker, *Int. Symp. Combust.*, **7**, 949 (1959).

20) G. B. Skinner and E. M. Sokoloski, *J. Phys. Chem.*, **64**, 1952 (1960).

21) C. F. Aten and E. F. Greene, *Combust. Flame*, **5**, 55 (1961).

22) T. Asaba, K. Yoneda, and T. Hikita, *Nippon Kogyo Kagaku Zasshi*, **64**, 47 (1961).

23) J. N. Bradley and G. B. Kistiakowsky, *J. Chem. Phys.*, **35**, 264 (1961).

24) G. I. Kozlov and V. G. Knorre, *Combust. Flame*, **6**, 253 (1962).

25) I. D. Gay, G. B. Kistiakowsky, J. V. Michael, and H. Niki, *J. Chem. Phys.*, **43**, 1720 (1965).

26) I. L. Mar'yasin and Z. A. Nabutovskii, *Kinet. Katal.*, **11**, 856 (1970).

27) W. H. Beck and J. C. Mackie, *J. Chem. Soc., Faraday Trans. 1*, **71**, 1363 (1975).

28) A. F. Bopp and R. D. Kern, *J. Phys. Chem.*, **79**, 2579 (1975).

29) A. S. Kalland, J. H. Purnell, and B. C. Shurlock, *Proc. R. Soc. London, Ser. A*, **300**, 120 (1967); M. C. Lin, *Can. J. Chem.*, **44**, 1237 (1968); M. L. Boyd, T. M. Wu, and M. H. Back, *ibid.*, **46**, 2415 (1968); G. B. Skinner, R. C. Sweet, and S. K. Davis, *J. Phys. Chem.*, **75**, 1 (1971); M. P. Schuchmann and K. J. Laidler, *Int. J. Chem. Kinet.*, **4**, 491 (1972).

30) S. W. Benson and G. R. Haugen, *J. Phys. Chem.*, **71**, 1735 (1967); *ibid.*, **71**, 4404 (1967).

31) M. Tsuda and K. Kuratani, *Bull. Chem. Soc. Jpn.*, **41**, 53 (1968).

32) M. Yamashita, Y. Sano, T. Tanaka, H. Ogura, and K. Kuratani, *Tokyo Daigaku Uchu Koku Kenkyusho Hokoku*, **11**, 545 (1975).

33) "JANAF Thermochemical Tables," 2nd ed, National Bureau of Standards NSRDS-NBS 37, U. S. Goverment Printing Office, Washington D. C., 1971.

34) M. Nakagawa and T. Inui, *Nippon Kagaku Zasshi*, **73**, 143 (1952).

35) G. F. Hennion, C. C. Price, and T. F. Mckeon, Jr., *J. Am. Chem. Soc.*, **76**, 5494 (1945).

36) M. H. Back, *Can. J. Chem.*, **49**, 2119 (1971).

37) M. Cowperwaite and S. H. Bauer, *J. Chem. Phys.*, **36**, 1743 (1962).

38) F. P. Lossing, *Can. J. Chem.*, **49**, 357 (1971).

39) The heat of formation of C_6H_5 radical was calculated as a rough approximation from that of C_6H_6 (straight chain) estimated by Westbrook *et al.*,[8] supposing the bond dissociation energy of the C–H bond in C_6H_6 is 104 kcal/mol.

40) The heat of formation of 2-ethynylvinyl radical is estimated to be 123.4 kcal/mol, when the bond dissociation energy of the C–H is taken equal to 40 kcal/mol.[36]

41) R. F. Stamm, F. Halverson, and J. J. Whalen, *J. Chem. Phys.*, **17**, 104 (1949).

42) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **1**, 221 (1969).

43) "Kinetic Data on Gas Phase Unimolecular Reactions," S. W. Benson and H. E. O'Neal, National Bureau of Standards NSRDS-NBS 21, U. S. Goverment Printing Office, Washington D. C., 1970, p. 26.

44) Taking the collision diameter of C_2H_2 molecule as 4.56 Å, the classical collision frequency is estimated as $10^{14.48}$ $cm^3\ mol^{-1}\ s^{-1}$, which is about one order of magnitude smaller than the frequency factor of k_{16}.

45) G. J. Mains, H. Niki, and M. H. Wijinen, *J. Phys. Chem.*, **67**, 111 (1963).