Shock Tube Study of the H–D Exchange Reaction between Acetylene and Deuterium

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H–D exchange reaction between acetylene and deuterium has been investigated in a single-pulse shock tube in the temperature range 1200—1500 K. Empirically, in the C_2HD appearance the order with respect to acetylene was 0.25 ± 0.09, and that with respect to deuterium 1.14 ± 0.15. The rate constant of 1.39 th order for the C_2HD increase was obtained as; $k(cm^{1.17}\ mol^{-0.39}\ s^{-1})=(24.4\pm7.5)\times10^{11}exp((-51200\pm2400)/RT)$. The isotopic distributions of acetylene and hydrogen as determined by mass spectrometry suggest that C_2D_2 and H_2 are formed by the subsequent reactions of C_2HD and HD, respectively. A free-radical chain mechanism initiated by the same bimolecular reaction of acetylene, viz. $2C_2H_2\rightarrow C_4H_3+H$, as in the pyrolysis and hydrogenation of acetylene was proposed. A steady-state treatment of the proposed mechanism shows that the empirical rate and concentration dependence of the C_2HD increase are in line with those of the steady-state rate.

The H–D exchange reaction between acetylene and deuterium has been studied by several investigators. Shock tube techniques were employed in all the experimental studies.

Kuratani and Bauer[1] derived empirical power rate formulas by the analysis of the infrared emission profiles of C_2H_2 and C_2HD, and proposed that C_2HD and C_2D_2 were produced from the same molecular complex C_2-H_2D_2*. Besides, Bauer et al.[2-4] discussed the structure and thermodynamic property of $C_2H_2D_2$*.

Gay et al.[5] studied the pyrolysis of acetylene combining a shock tube with a TOF mass spectrometer and found C_4H_3 radical. They proposed a radical mechanism for the isotopic exchange reaction between C_2H_2 and C_2D_2, suggesting that this might be the case for the H–D exchange reaction between C_2H_2 and D_2.

Benson and Haugen[6] proposed a free-radical chain mechanism by the analysis of both kinetic and thermodynamic data available. By a single-pulse shock tube Skinner et al.[7] studied the reaction of the C_2H_2–D_2 system in the temperature range 1069—1280 K. They found that the amount of C_2D_2 was less than one half of C_2HD amount, C_2H_3D being the most abundant among ethylene isomers. From these observations, they supported the radical chain mechanism postulated by Benson and Haugen, but did not execute the quantitative analysis of kinetic date obtained.

The pyrolysis and hydrogenation of acetylene proceed via the free-radical chain mechanism initiated by the same bimolecular reaction of acetylene; $2C_2H_2\rightarrow C_4H_3+H$, C_4H_3 radical being responsible for the formation of 1-buten-3-yne and H atom for the production of ethylene.[8] On the other hand, the H atom could also lead to the H–D exchange reaction between acetylene and deuterium in the C_2H_2–D_2 system. As in the pyrolysis and hydrogenation of acetylene, the H–D exchange between acetylene and deuterium would occur by a free-radical chain mechanism. The study of the H–D exchange reaction in the C_2H_2–D_2 system could provide another test for the mechanism of hydrogenation of acetylene.

Experimental

Apparatus and Procedure. The H–D exchange reaction between acetylene and deuterium was investigated in a 4-cm

single-pulse shock tube. A full description of the shock tube and the details of operation have been given previously.[8,9]

Shock tube was evacuated to below 1×10^{-4} Torr before each run, leak and outgassing rate being ca. 6×10^{-5} Torr/min. Prior to the opening of the tube for the renewal of the diaphram, the entire tube was pressurized with helium above the atmospheric pressure to avoid the exposure of the tube to the air. The shocks were fired within five minutes after the introduction of sample gases. Helium was used as the driver gas.

Materials. Three 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. The mixed gases were allowed to stand at a room temperature for about one day and analyzed by gas chromatography to check trace amount of oxygen prior to shock heating. All analyses showed that the oxygen in the sample mixtures was less than 10 ppm. The procedure of purification of acetylene, deuterium, and argon was identical with that in the pyrolysis and hydrogenation experiments.

Analytical. The isotopic distribution of acetylene was determined with a Hitachi Model RM-50 mass spectrometer. Details of the mass spectral analyses were described elsewhere. In some runs the isotopic distribution of hydrogen was determined at the same time. For this purpose, the bulb containing sample gas was condensed by liquid nitrogen, while the uncondensables were transferred into another evacuated bulb, which served for the measurement of the isotopic distribution of hydrogen. The removal of hydrocarbons by the procedure mentioned above could minimize the interference in the hydrogen peaks due to the fragmentation of the hydrocarbons. The relative intensity among the hydrogen isotopes was determined using an equilibrium mixture of hydrogen isotopes, which was prepared by platinum-black catalyzed reaction between H_2 and D_2.

Results

Three mixtures were subjected to shock heating in the temperature range 1000—1600 K, and then analyzed by mass spectrometry. The total densities behind the reflected shock waves were $(2.35\pm0.11)\times10^{-5}$ mol/cm^3, the average reaction time(dwell time) being ca. 800 μs in all runs.

Isotopic Distributions. Several shocks were fired with the mixture of 10% C_2H_2 and 10% D_2 in argon. The isotopic distribution of hydrogen together with that of acetylene was determined by mass spectrometry. The ionization potential was maintained at 50 eV for the

TABLE 1. ISOTOPIC DISTRIBUTIONS OF ACETYLENE AND HYDROGEN

$T_5/K^{a)}$	$C_2H_2{}^{b)}$	C_2HD	C_2D_2	$D_2{}^{b)}$	HD	H_2	$\tau/\mu s^{c)}$
1271	0.946	0.051	0.003	0.954	0.044	0.002	920
1313	0.932	0.067	0.001	0.934	0.060	0.006	940
1388	0.894	0.102	0.004	0.888	0.095	0.017	930
1395	0.908	0.087	0.005	0.904	0.093	0.003	850
1396	0.886	0.110	0.004	0.882	0.111	0.006	890
1480	0.763	0.214	0.023	0.743	0.231	0.026	780

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

measurement of hydrogen isotope mass spectra, while at *ca.* 12 eV for that of acetylene isomers. The results of mass spectral analyses are summarized in Table 1.

As shown in Table 1, approximately equal amounts of C_2HD and HD, and those of C_2D_2 and H_2 are produced, the yields of the latter being much less than one half of the former.

Rate of H–D Exchange Reaction.   The relative amounts of acetylene isomers were determined throughout all runs. In this case the ionization potential was kept at 50 eV. The rates of C_2HD and C_2D_2 appearance were derived from the relative amounts of acetylene isomers, neglecting the decrease of the total acetylene concentrations due to the pyrolysis and hydrogenation of acetylene occurring simultaneously with the H–D exchange reaction. The rates were defined as $[C_2HD]$ /τ and $[C_2D_2]/\tau$, where τ is the dwell time. The rates at temperatures below 1200 K were too slow to allow a quantitative analysis and were ruled out   The rates of the H–D exchange reaction of acetylene are shown in Fig. 1 in the case of the mixture of $C_2H_2/D_2/Ar=$ 5/10/85. The rates of C_2HD appearance increase linearly with temperature at temperatures below 1400 K, while they deviate from a linear line at temperatures above 1400 K. The ratio of $[C_2D_2]/[C_2HD]$ is dependent on temperature. This indicates that the formation of C_2D_2 by the subsequent reaction of C_2HD and the reverse reaction of C_2HD to reform C_2H_2 cannot

Fig. 1. Rates of the C_2HD and C_2D_2 increase in the case of the mixture of $C_2H_2/D_2/Ar=5/10/85$.
●; C_2HD increase, ○; C_2D_2 increase.

TABLE 2. ISOTOPIC DISTRIBUTION OF ACETYLENE AS DETERMINED WITH IONIZATION POTENTIAL OF 50 eV

$T_5/K^{a)}$	$C_2H_2{}^{b)}$	C_2HD	C_2D_2	$\tau/\mu s^{c)}$	$C_2H_2/D_2/Ar^{d)}$
1371	0.896	0.093	0.011	780	10/10/80
1380	0.900	0.091	0.009	810	10/10/80
1386	0.854	0.133	0.013	910	10/10/80
1473	0.701	0.259	0.040	770	10/10/80
1480	0.690	0.274	0.036	700	10/10/80

a) T_5 is the temperature behind the reflected shock wave.
b) The total amount of acetylene is normalized to be 1.000.
c) τ is the dwell time.   d) The composition of the mixture.

be neglected at temperatures above 1400 K for the mixture of $C_2H_2/D_2/Ar=5/10/85$.

The rates of C_2D_2 increase scatter considerably at lower temperatures. Some of the results of the relative yields of acetylene isomers for the mixture of C_2H_2/D_2 /Ar=10/10/80, as determined at an ionization potential of 50 eV, are presented in Table 2. Apparent greater C_2D_2 abundance in Table 2 may result from the contamination of nitrogen, since at the lower ionization potential of 12 eV the fragmentation of nitrogen can be neglected(Table 1). However, the relative yields of C_2HD seem little affected by the ionization potential employed. Thus the kinetic analysis of the data obtained was made only for the rates of C_2HD increase.

The rates of C_2HD appearance obtained from the three shock heated mixtures are shown in Fig. 2. We see that the rates of C_2HD formation are strongly dependent on deuterium and slightly dependent on acetylene concentration.

In the above definition of rate, the rates of C_2HD increase are well defined only when the successive exchange of C_2HD to C_2D_2 (alternatively C_2H_2) is negligibly slow. The rates of C_2D_2 formation were less than one tenth of those of C_2HD increase in the temperature range up to 1500 K in the mixtures of $C_2H_2/D_2/Ar=$ 10/10/80 and 10/5/85 and up to 1400 K for the mixture of $C_2H_2/D_2/Ar=5/10/85$.

An empirical power rate formula was derived by the least-squares method in the temperature range mentioned above, where the rates of C_2HD formation increase monotonically with temperature and successive exchange of C_2HD is negligibly slow:

$$d[C_2HD]/dt = k_1[C_2H_2]^{0.25\pm0.09}[D_2]^{1.14\pm0.15}, \qquad (1)$$

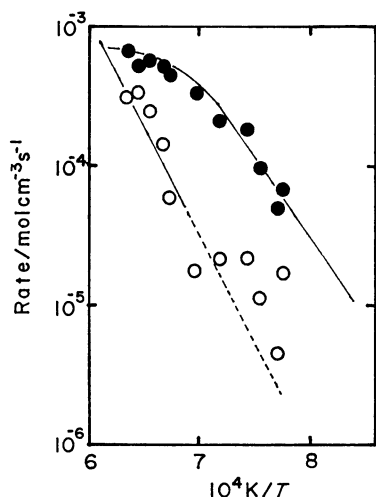$$k_1 = (24.4\pm7.5) \times 10^{11} \exp((-51200\pm2400)/RT), \qquad (2)$$
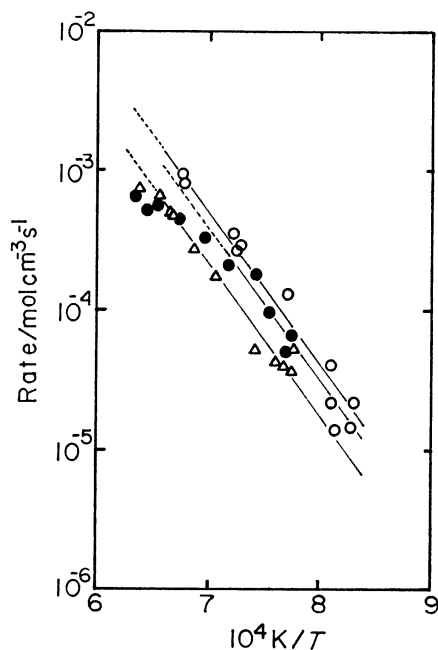
Fig. 2. Concentration dependence of the C_2HD increase.
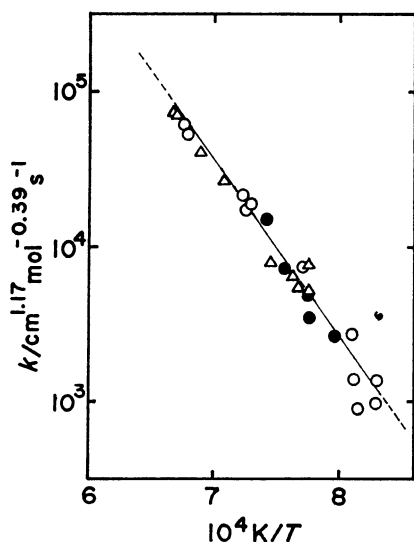○; $C_2H_2/D_2/Ar=10/10/80$, ●; $C_2H_2/D_2/Ar=5/10/85$,
△; $C_2H_2/D_2/Ar=10/5/85$.

Fig. 3. Arrhenius plot of 1.39th order rate constants for the C_2HD appearance.
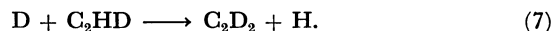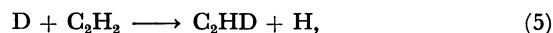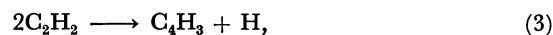○; $C_2H_2/D_2/Ar=10/10/80$, ●; $C_2H_2/D_2/Ar=5/10/85$,
△; $C_2H_2/D_2/Ar=10/5/85$.

where $d[C_2HD]/dt$ and k_1 are expressed in mol cm^{-3} s^{-1} and cm$^{1.17}$ mol$^{-0.39}$ s^{-1}, respectively, the activation energy being given in cal/mol. The errors denote the standard deviation of the least-squares method. The Arrhenius plots of the 1.39 th order rate constants are shown in Fig. 3.
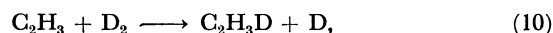
Discussion

Mechanism of H–D Exchange Reaction.   The isotopic distributions of acetylene and hydrogen(Table 1) are in line with those obtained by Skinner *et al.*,[7] who supported a free-radical chain mechanism. The very

low ratios of $[C_2D_2]/[C_2HD]$ and $[H_2]/[HD]$, and the dependence of the former on temperature suggest that C_2D_2 and H_2 are produced successively by the reactions of C_2HD and HD, respectively.

Under the present experimental conditions, the H–D exchange reaction occurs simultaneously with the pyrolysis and hydrogenation of acetylene, the pyrolysis being predominant. The initiation step of the pyrolysis becomes an important source of radicals. The most probable free-radical chain mechanism for the H–D exchange reaction is outlined as follows:

$$2C_2H_2 \longrightarrow C_4H_3 + H, \tag{3}$$
$$H + D_2 \longrightarrow HD + D, \tag{4}$$
$$D + C_2H_2 \longrightarrow C_2HD + H, \tag{5}$$
$$H + HD \longrightarrow H_2 + D, \tag{6}$$
$$D + C_2HD \longrightarrow C_2D_2 + H. \tag{7}$$

The H and D atoms present in the system concurrently participate in the formation of ethylenes:

$$H + C_2H_2 \longrightarrow C_2H_3, \tag{8}$$
$$D + C_2H_2 \longrightarrow C_2H_2D, \tag{9}$$
$$C_2H_3 + D_2 \longrightarrow C_2H_3D + D, \tag{10}$$
$$C_2H_2D + D_2 \longrightarrow C_2H_2D_2 + D. \tag{11}$$

The termination occurs by the recombination or disproportionation reactions of the two vinyl radicals or by those of vinyl radicals with H or D atom.
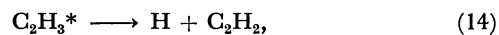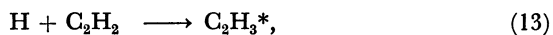
A molecular complex mechanism was proposed by Kuratani and Bauer, which was essentially expressed as;

$$C_2H_2 + D_2 \longrightarrow C_2H_2 : D_2 \longrightarrow C_2H_2D_2{}^*, \tag{12}$$
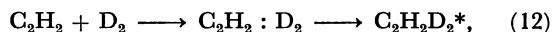
where $C_2H_2 : D_2$ and $C_2H_2D_2{}^*$ were suggested to be the carbene and excited ethylene with V_d symmetry, respectively. In their scheme the $C_2H_2D_2{}^*$ rotates around the C=C bond to $C_2HD : HD$ or $C_2D_2 : H_2$ (alternatively $C_2H_2 : D_2$), and then decompose to C_2HD or C_2D_2. Accordingly, the ratios of $[C_2D_2]/[C_2HD]$ and $[H_2]/[HD]$ would be *ca.* 0.5 and would be substantially independent of temperature. These predictions from the molecular complex mechanism disagree with the observed isotopic distributions.[10]

Steady-state Rate.   In the proposed mechanism the successive exchange reactions of C_2HD and HD and the backward reactions except for Reactions 8 and 9 can be neglected in the early stage of the exchange reaction, since the reaction times were extremely short, the yields of C_2D_2 and H_2 being far less than those of C_2HD and HD in the temperature range defined above. Reactions 9 and 11 can be also neglected, since C_2H_3D was the most predominant species among ethylene isomers.[8]

It is well known that the addition of H atom to acetylene yields vibrationally excited vinyl radical with subsequent dissociation to initial reactants or collisional stabilization to form thermal vinyl radical;[11–14]
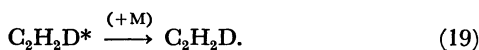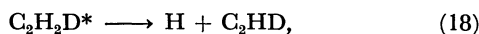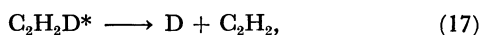
$$H + C_2H_2 \longrightarrow C_2H_3{}^*, \tag{13}$$
$$C_2H_3{}^* \longrightarrow H + C_2H_2, \tag{14}$$
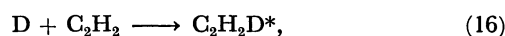$$C_2H_3{}^* \xrightarrow{(+M)} C_2H_3, \tag{15}$$

where $C_2H_3{}^*$ and M are vibrationally excited vinyl

radical and a third body, respectively. Reactions 13—15 overall reduce to

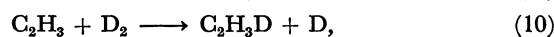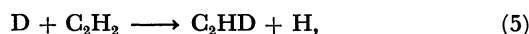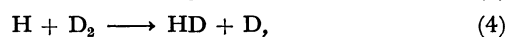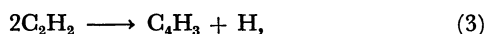$$H + C_2H_2 \rightleftharpoons C_2H_3, \qquad (8')$$
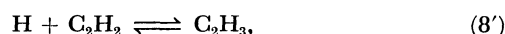
where the reverse reaction is included, since C_2H_3D was formed in a considerable amount. In the case of the addition of D atom to C_2H_2, the above processes become as follows:[12,14]

$$D + C_2H_2 \longrightarrow C_2H_2D^*, \qquad (16)$$

$$C_2H_2D^* \longrightarrow D + C_2H_2, \qquad (17)$$

$$C_2H_2D^* \longrightarrow H + C_2HD, \qquad (18)$$

$$C_2H_2D^* \xrightarrow{(+M)} C_2H_2D. \qquad (19)$$

Practically, these steps reduce to Reactions 5 and 9. The reverse Reaction 9 can be neglected, for the yield of $C_2H_2D_2$ was small relative to C_2H_3D yield. Reactions 8 and 9 involve thermalized vinyl radicals, while in Reaction 5 the dissociation of the "hot" vinyl radical is significant. The formation of thermal vinyl radical from "hot" vinyl radical under our experimental conditions is estimated to be slow compared with exchange.[6]

As in the hydrogenation of acetylene, the termination reaction of H atom with C_2H_3 radical is insignificant, since the concentration of H atom is much lower than that of C_2H_3 radical. The simplified free-radical chain mechanism for the $C_2HD(HD)$ appearance is thus represented as:

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

$$H + D_2 \longrightarrow HD + D, \qquad (4)$$

$$D + C_2H_2 \longrightarrow C_2HD + H, \qquad (5)$$

$$H + C_2H_2 \rightleftharpoons C_2H_3, \qquad (8')$$

$$C_2H_3 + D_2 \longrightarrow C_2H_3D + D, \qquad (10)$$

$$2C_2H_3 \longrightarrow C_4H_6. \qquad (20)$$

For the termination, only the recombination reaction of two vinyl radicals is taken into account.

The steady-state assumption is applied to the simplified mechanism. The steady-state concentrations of H, D, and C_2H_3 radical are given by the following equations;

$$[C_2H_3]_{ss} = (k_3/2k_{20})^{1/2}[C_2H_2] = k_{21}[C_2H_2], \qquad (21)$$

$$[H]_{ss} = (1/k_{8'})(k_3[C_2H_2] + k_{-8'}k_{21} + k_{10}k_{21}[D_2]), \qquad (22)$$

$$[D]_{ss} = (1/k_5[C_2H_2])(k_4[H]_{ss}[D_2] + k_{10}[C_2H_3]_{ss}[D_2]), \qquad (23)$$

where $k_{21}=(k_3/2k_{20})^{1/2}$. Rearranging Eq. 23, the following relation is derived:

$$d[C_2HD]/dt = d[HD]/dt + d[C_2H_3D]/dt \qquad (23')$$

The rate of C_2H_3D formation is slower than that of HD increase. The rate of HD increase is approximately equal to that of C_2HD appearance, which is consistant with the observed isotopic distributions (Table 1). Thus the steady-state rate for C_2HD increase is given by

$$d[C_2HD]/dt = d[HD]/dt = k_4[H]_{ss}[D_2]. \qquad (23'')$$

Equation 23'', if reduced to a power dependence on concentrations, predicts order with respect to acetylene and deuterium of 0 to 1 and 1 to 2, respectively.

The rate constants used in the derivation of an appar-

TABLE 3. THE RATE CONSTANTS RELATING TO THE H–D EXCHANGE REACTION AND THE FORMATION REACTION OF ETHYLENE

Reaction	Rate constant $(s^{-1}$ or $cm^3\,mol^{-1}\,s^{-1})$	Ref.	$\lambda^{a)}$
3	$3.5 \times 10^{13} \exp(-47400/RT)$	9	1.0
4	$6.5 \times 10^{13} \exp(-8560/RT)$	15	2.0
5	$3.1 \times 10^{13} \exp(-3700/RT)$	12	1.0
8'	$7.53 \times 10^{11} \exp(-2410/RT)$	13	1/7.2
−8'	$8.19 \times 10^{11} \exp(-50210/RT)$	b)	1/7.2
10	$5.39 \times 10^{11} \exp(-12900/RT)$	8	1.0
20	4.45×10^{12}	c)	1.0

a) λ is the correction factor for the frequency factor with the same activation energy as that given in the reference. b) This rate constant was calculated by the combination of the rate constant of Reaction 8' with the equilibrium constant at 1300 K. c) The activation energy was assumed to be zero, and the frequency factor was calculated at 1300 K, taking the collision diameter of C_2H_3 radical as 4.23 Å.

ent power rate formula for the C_2HD increase are listed in Table 3. The pressure dependent bimolecular rate constant of Reaction 8' is uncertain. The rate constant is assumed to have the same activation energy as that in high pressure limit with a correction in frequency factor.[13] Assuming the same activation energy as that of the observed rate (Eq. 2), an apparent power rate formula for the C_2HD increase is given by

$$d[C_2HD]/dt(mol\,cm^{-3}\,s^{-1}) = k_{24}[C_2H_2]^{0.31}[D_2]^{1.39}, \qquad (24)$$

$$k_{24}(cm^{2.10}\,mol^{-0.70}\,s^{-1}) = 1.16 \times 10^{14} \exp(-51200/RT). \qquad (25)$$

The absolute values of the steady-state rate agree with those of the empirical power rate (Eqs. 1 and 2) within the error limit of 40%, and the power dependence of the steady-state rate is in good agreement with the observed rate within the present experimental errors.

The empirical power rate expression for the increase of C_2HD obtained by Kuratani and Bauer in the temperature range 1300—1600 K is given by

$$d[C_2HD]/dt = ((k_\alpha + k_\beta)/2.64)[C_2H_2]^{0.24}[D_2]^{1.0}, \qquad (26)$$

where,

$$k_\alpha(cm^{0.72}\,mol^{-0.24}\,s^{-1}) = 4.2 \times 10^8 \exp(-33800/RT)$$

and

$$k_\beta(cm^{0.72}\,mol^{-0.24}\,s^{-1}) = 1.6 \times 10^8 \exp(-29300/RT).$$

The dependence of the rates on the concentrations seems essentially the same between the two power rate expressions (Eqs. 1 and 26), in spite of the different definition of rate, that is, their rates are the initial rates, on the other hand, our rates are the mean rates during the reaction times. The absolute rates obtained by them and those of the present agree within a factor of 2.

The steady-state rate of C_2H_3D production is directly derived from Eq. 21;

$$d[C_2H_3D]/dt(mol\,cm^{-3}\,s^{-1}) = k_{10}k_{21}[C_2H_2][D_2], \qquad (27)$$

where,

$$k_{10}k_{21}(cm^3\,mol^{-1}\,s^{-1}) = 1.3 \times 10^{12} \exp(-36600/RT). \qquad (28)$$

Equation 27 indicates that as far as the rate of Reaction 8' is fast enough to reach a steady-state concentration of C_2H_3 radical during the reaction time, the rates of Reactions 8' and $-8'$ do not produce any change in the rate of ethylene formation together with the steady-state concentration of C_2H_3 radical (Eq. 21). However, the steady-state concentration of H(D) atom is affected by the rates of Reactions 8' and by the rates of Reaction 8' and its reverse reaction (Eq. 22). This indicates that the H–D exchange reaction is closely related to the C_2H_3 radical formation and ethylene formation. The following relation may hold well:[8]

$$[C_2H_3D]/[C_2H_2D_2] = (k_{10}/k_{11})([C_2H_3]/[C_2H_2D])$$

$$= (k_{8'}/k_9)([H]/[D])$$

$$= (k_5/k_4)([C_2H_2]/[D_2]). \qquad (29)$$

In the above derivation, $k_{8'} = k_9$ and $d[HD]/dt \gg d[C_2H_3D]/dt$ are assumed. The ratios of $[C_2H_3D]/[C_2H_2D_2]$, observed and calculated from Eq. 29, are summarized in Table 4. The agreement between the observed and calculated appears considerably good. Therefore, the inclusion of H–D exchange propagation process into the ethylene formation scheme provides a reasonable explanation of the rate and isotopic distribution of ethylene.

TABLE 4. THE COMPARISON OF THE OBSERVED RATIO OF $[C_2H_3D]/[C_2H_2D_2]$ WITH THE CALCULATED VALUE

$T_5/K^{a)}$	$[C_2H_3D]/[C_2H_2D_2]$		$\gamma^{c)}$	$C_2H_2/D_2/Ar^{d)}$
	Obsd[b]	Calcd		
1271	5.86	2.90	2.02	10/10/80
1313	5.68	2.74	2.08	10/10/80
1388	3.86	2.49	1.55	10/10/80
1407	3.76	2.44	1.54	10/10/80
1480	1.89	2.25	0.84	10/10/80

a) T_5 is the temperature behind the reflected shock wave. b) Calculated value from Table 2 in Ref. 8. c) γ is the ratio of the observed value to the calculated one from Eq. 29. d) The composition of the mixture.

At temperatures above 1500 K, the formation of 1,3-butadiyne becomes comparable to that of ethylene or predominant. The butadiyne formation cannot be neglected in the H–D exchange reaction, since H atom is responsible simultaneously for the butadiyne formation:[9]

$$H + C_2H_2 \longrightarrow C_2H + H_2, \qquad (30)$$

$$C_2H + C_2H_2 \longrightarrow C_4H_2 + H. \qquad (31)$$
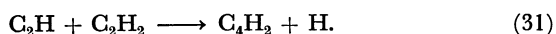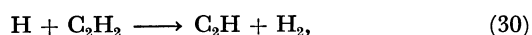
D atom present in the system can abstract H atom from acetylene molecule:

$$D + C_2H_2 \longrightarrow HD + C_2H, \qquad (32)$$

$$C_2H + D_2 \longrightarrow C_2HD + D. \qquad (33)$$
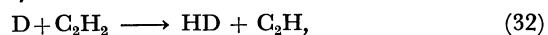
Reactions 32 and 33 construct a chain for the H–D exchange reaction between acetylene and deuterium. Furthermore, the yield of 1-buten-3-yne begins to decrease at temperatures around 1500 K, H atom being supposed to participate in the 1-buten-3-yne decrease. The validity of our mechanism should be limited to the temperature range where the formation of 1-buten-3-yne and ethylene is dominant and that of butadiyne is negligibly slow.

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10) Bauer et al.[4] explained the observed low ratio of $[C_2D_2]/[C_2HD]$ by the accompanied self-exchange reaction between C_2H_2 and C_2D_2 such as; $C_2H_2 + C_2D_2 \rightarrow 2C_2HD$. In our pyrolysis experiments of 5% equimolar mixture of C_2H_2 and C_2D_2, however, the mass spectrometric analysis of acetylene isomers showed that the amount converted into C_2HD was at most 10% of the initial acetylene concentration.[9]

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