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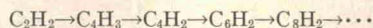
## Thermal Decomposition of Acetylene in Shock Waves

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Using a shock tube and an improved T.O.F. mass spectrometer displaying spectra every 20  $\mu$ sec, the pyrolysis of acetylene was shown to proceed through the sequence



in the temperature range 1600°–2400°K. All these intermediates reach steady-state concentrations, that of the radical  $\text{C}_4\text{H}_3$  being as large as that of diacetylene under favorable conditions. The primary bimolecular reaction of acetylene in which the radical  $\text{C}_4\text{H}_3$  is formed must also yield hydrogen atoms. These catalyze an isotopic exchange in mixtures of  $\text{C}_2\text{H}_2 + \text{C}_2\text{D}_2$  that is about three orders of magnitude faster than the formation of  $\text{C}_4\text{H}_2$ . The initial yield of acetylene- $d_1$  is given by the expression

$$[\text{C}_2\text{HD}]_t = k[\text{C}_2\text{H}_2 + \text{C}_2\text{D}_2]_0^{3/2},$$

which is consistent with the proposed partial reaction mechanism. The mechanism of conversion of  $\text{C}_4\text{H}_3$  into  $\text{C}_4\text{H}_2$ , etc., is uncertain but undoubtedly involves free radicals.

### INTRODUCTION

THE pyrolysis of acetylene has been studied extensively. At lower temperatures conventional static methods have been used.<sup>1-3</sup> Flow reactor techniques were employed to explore the intermediate temperature

range,<sup>4-10</sup> while shock waves served to observe the re-

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<sup>1</sup> G. J. Minkoff, D. M. Newitt, and P. Rutledge, *J. Appl. Chem.* **7**, 406 (1957).

<sup>2</sup> G. J. Minkoff, *Can. J. Chem.* **36**, 131 (1958).

<sup>3</sup> C. G. Silcocks, *Proc. Roy. Soc. (London)* **A242**, 411 (1957).

<sup>4</sup> F. C. Stehling, J. D. Frazee, and R. C. Anderson, *Symp. Combust.*, 6th, Yale Univ. 1956, 247 (1957).

<sup>5</sup> F. C. Stehling, J. D. Frazee, and R. C. Anderson, *Symp. Combust.*, 8th, Pasadena, Calif. 1960, 775 (1962).

<sup>6</sup> M. S. B. Muson and R. C. Anderson, *Carbon* **1**, 51 (1963).

<sup>7</sup> C. D. Towell and J. J. Martin, *Am. Inst. Chem. Engr. J.* **7**, 693 (1961).

<sup>8</sup> C. R. Kinney and R. S. Slysh, *Proc. 4th Carbon Conf. Oxford* 301 (1960).

<sup>9</sup> H. B. Palmer and F. L. Dormish, *J. Phys. Chem.* **66**, 1553 (1964).

<sup>10</sup> C. F. Cullis and N. H. Franklin, *Proc. Roy. Soc. (London)* **A280**, 139 (1964).

action at the highest temperatures.<sup>11-15</sup> The activation energies and the pre-exponential factors vary substantially among different investigators, but the absolute values of the rate constants in these publications show a very satisfactory consistency. The initial reaction has been definitely shown to be second order in acetylene, although there are some dissents.<sup>14</sup>

The chemical course of the reaction is less clear. Most authors agree that the final products are carbon and hydrogen. However, polyaromatic compounds as well as substances with the empirical formula  $(C_2H_2)_n$  have been observed at lower temperatures.<sup>3</sup> Vinyl acetylene has been reported in experiments that employ the static, flow reactor, and shock tube techniques. However, Aten and Greene<sup>13</sup> find diacetylene to be the only  $C_4$  intermediate with a shock tube.

The work described here is an extension of the experiments of Bradley and Kistiakowsky (B and K)<sup>14</sup> who used a shock tube and a T.O.F. mass spectrometer, but the present work was carried out with vastly improved equipment<sup>16-18</sup> and has led to different conclusions.

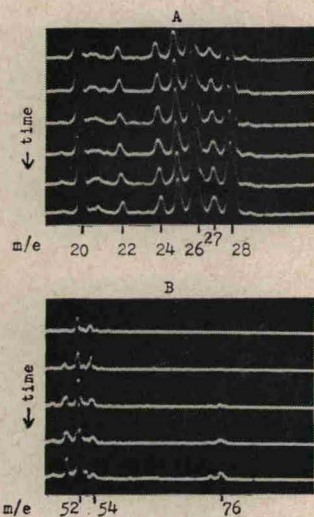


FIG. 1. (A) A few consecutive spectra at intervals of 20  $\mu$ sec, beginning 120  $\mu$ sec from reflection of shock showing the formation of  $C_2HD$  ( $m/e=27$ ) in an equimolar mixture of  $C_2H_2$  and  $C_2D_2$  in neon at 1425°K; (B) A few consecutive spectra at 2200°K showing the formation of  $C_4D_2$  ( $m/e=54$ ) and slower formation of  $C_4D_2$  ( $m/e=52$ ) and  $C_6D_2$  ( $m/e=76$ ).

<sup>11</sup> W. J. Hooker, Symp. Combust., 7th, London and Oxford 1958, 949 (1959).

<sup>12</sup> G. B. Skinner and E. M. Sokoloski, J. Phys. Chem. **64**, 1952 (1960).

<sup>13</sup> C. F. Aten and E. F. Greene, Combust. Flame **5**, 55 (1961).

<sup>14</sup> J. N. Bradley and G. B. Kistiakowsky, J. Chem. Phys. **35**, 264 (1961).

<sup>15</sup> G. I. Kozlov and V. G. Knorre, Combust. Flame **6**, 253 (1962).

<sup>16</sup> J. E. Dove and D. McL. Moulton, Proc. Roy. Soc. (London) **A283**, 216 (1965).

<sup>17</sup> G. P. Glass, G. B. Kistiakowsky, J. V. Michael, and H. Niki, J. Chem. Phys. **42**, 608 (1965).

<sup>18</sup> D. McL. Moulton and J. V. Michael, Rev. Sci. Instr. **36**, 226 (1965).

## EXPERIMENTAL

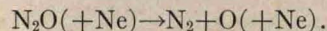
Hydrogen was used in the shock tube as the driver gas and neon as the inert diluent. The acetylene content varied from 2.5% to 17%. Compression factors by the reflected shock were 40 to 70 with initial total ambient pressures of 5 to 7.5 Torr. Acetylene, acetylene- $d_2$ , and their equimolar mixtures were used in various experiments. Acetylene, from Matheson Company, was purified by fractional bulb-to-bulb vacuum distillation. Acetylene- $d_2$ , from Merck, Sharp & Dohme Ltd. of Canada, was used as received. So was neon, from Matheson Company, which had a stated purity of 99.99%, the impurity being mostly helium.

Temperatures and densities in the reflected shock waves were calculated from the velocities of the incident waves by the previously developed programs<sup>16</sup> for an IBM 1620 computer.

The energy of ionizing electrons in the T.O.F. mass spectrometer was kept at 34 eV, and mass spectra were obtained every 20  $\mu$ sec. A chemi-ion suppressor grid that has been developed since our last publication was used. With this addition the mass spectra are exceptionally free from random noise and quantitative peak-height measurements are more reliable. Also the random fluctuations of peak heights were substantially reduced by improving the sensitivity of the T.O.F. mass spectrometer. Some typical spectra are shown in Fig. 1. Peak heights were assumed to be proportional to concentrations in the course of each run. The mass spectra showed resolution of adjacent ( $\Delta m/e=1$ ) mass peaks up to about  $m/e=100$ . The mass calibration for unknown species was made with benzene fragment ions as mass markers and the scale was extended to higher masses by the relation: time of flight =  $c(m/e)^{1/2}$ . Measurements of ion mass shifts when acetylene- $d_2$  was substituted for acetylene gave unambiguous assignments up to mass 100. A re-entrant conical orifice<sup>17</sup> which connected the shock tube and the T.O.F. was used in all experiments.

## RESULTS

To explore further<sup>17</sup> the extent to which reflected waves are nonideal and the boundary layer interferes with the observations of reactions within the shock tube, fairly extensive measurements were made on the initial stages of the reaction



Quite reliable high-temperature data are now available<sup>19</sup> for this reaction. Figure 2 shows the plot of our observed pseudo first-order rate constants and a line which was obtained by Fishburne and Edse at a somewhat higher concentration of  $N_2O$  and argon diluent. Since the reaction under these conditions is actually second order, the agreement of our data with those obtained by different techniques is most gratifying and

<sup>19</sup> E. S. Fishburne and R. Edse, J. Chem. Phys. **41**, 1297 (1964).

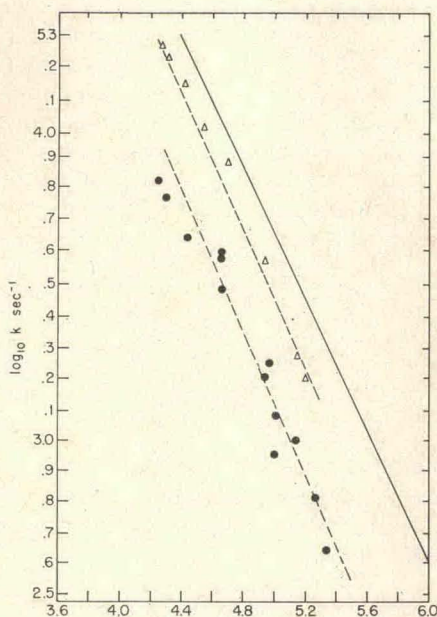


FIG. 2. Observed pseudo first-order rate constants of nitrous oxide decomposition in 5% mixtures with neon. Solid circles:  $2 \times 10^{-6}$  mole/cc total; triangles:  $3 \times 10^{-6}$  mole/cc; solid line: data of Fishburne and Edse at  $1.3 \times 10^{-5}$  mole/cc total concentration.

justifies giving considerable credence to quantitative measurements of mass spectra obtained with the T.O.F. mass spectrometer. However, as in earlier work,<sup>17</sup> it was observed that after about 500  $\mu$ sec from the instant of reflection of the shock wave the reaction began to slow down and stopped before  $N_2O$  was all decomposed. The explanation is that colder gas from the boundary layer becomes a substantial and growing fraction of the total gas flow into the T.O.F. mass spectrometer and this makes quantitative measurements meaningless.

B and K reported that acetylene concentration decreased only to 0.7 to 0.9 of the initial value, and became stationary thereafter. This was undoubtedly due to the boundary layer effect just described which must have been more severe in their experiments. We have been able to observe a roughly second-order decrease of the acetylene mass peak down to only 0.3 of the initial peak when the reaction was fast enough, i.e., at about 2200°K with our experimental conditions. Regardless of the rate of disappearance the reaction seemed to cease after about 500  $\mu$ sec, perhaps longer at lower temperatures, that is at about the same elapsed time as in the nitrous oxide decomposition. This induced us to concentrate on the early stages of the reaction during which the change in acetylene concentration was on the average not large.

To obtain sufficient resolution of the product mass peaks the spectrum was expanded in most runs and the acetylene peak was off the CRT faces. The following products were observed and unambiguously identified by the use of acetylene- $d_2$ :  $H_2$ ,  $C_4H_2$ ,  $C_4H_3$ ,  $C_6H_2$ ,

and  $C_8H_2$ . A  $C_{10}$  species which is likely to be  $C_{10}H_2$  was observed at high temperatures. In the paper of B and K a single peak at  $m/e = 51.4 \pm 0.4$  was reported. It was undoubtedly the unresolved doublet of  $C_4H_2$  and  $C_4H_3$  since vinyl acetylene,  $m/e = 52$ , was not observed in any of the present runs. Melton and Hamill<sup>20</sup> have found  $C_4H_2^+$  and  $C_4H_3^+$  to be the major products of ion-molecule reactions of acetylene in the ion source of a T.O.F. mass spectrometer. To determine whether this is the origin of the observed mass peaks 50 and 51, acetylene was introduced into the ion source of the T.O.F. mass spectrometer in steady flow experiments. With gas flow conditions into the T.O.F. approximately the same as in a shock-wave experiment, virtually no ions of mass 50 and 51 were observed. At much higher acetylene concentrations in the ion source small peaks at these masses were indeed observed. The yield of these ions is so small, however, that in the shock-wave experiments the mass peaks of  $C_4H_2^+$  and  $C_4H_3^+$  can be with certainty ascribed to the neutral species,  $C_4H_2$  and  $C_4H_3$ , streaming into the T.O.F. mass spectrometer.

On the basis of many experiments it can definitely be stated that  $C_4H_3$  appears earliest and first reaches a steady-state concentration; it is followed by  $C_4H_2$ ,  $C_6H_2$ , and  $C_8H_2$  in that order, rather than simultaneously, and each attains a steady state and then decays as acetylene is depleted. Figures 3 and 4 show the peak heights of the product species at about 2000° and 2200°K, respectively. The former clearly shows the induction period and the attainment of the steady state for  $C_4H_2$ , while the latter illustrates mainly the formation of  $C_6H_2$  and  $C_8H_2$ . Molecular hydrogen was detected only after the formation of substantial quantities of  $C_4H_2$ ; small peak heights prevented quantitative measurements. The spectrometer was not sufficiently sensitive for the detection of atomic hydrogen.

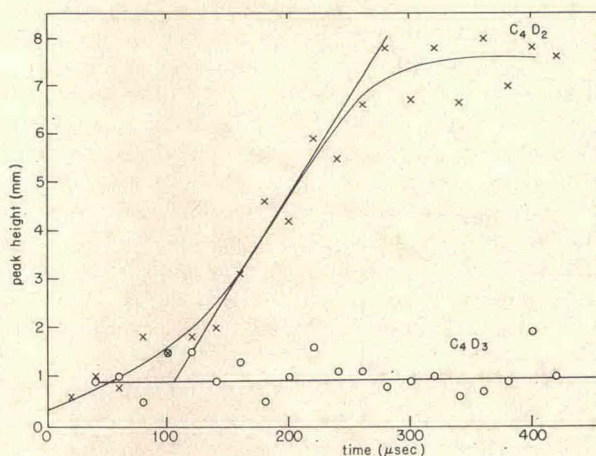


FIG. 3. Formation of intermediates at 2000°K in a 10% mixture of  $C_2D_2$  and neon at  $2.2 \times 10^{-6}$  mole/cc total concentration.

<sup>20</sup> C. E. Melton and W. H. Hamill, J. Chem. Phys. **41**, 1469 (1964).

Table I shows the peak heights of  $C_4D_2$  and  $C_4D_3$  after they reach steady-state concentration. Each value is the average of six to 12 consecutive spectra in one experiment. The sensitivity of the mass spectrometer could have varied somewhat from one experiment to another, and therefore the ratio  $(C_4H_2)/(C_4H_3)$  may be a more accurate measure of relative concentrations. The steady-state concentration of the radical  $C_4H_3$  is attained too fast to permit quantitative measurements of the rate of its formation. The rate of formation of  $C_4H_2$  shows usually a significant initial acceleration, or an induction period, whose duration is about the same as the time required for the concentration of  $C_4H_3$  to reach an approximately steady state. Because

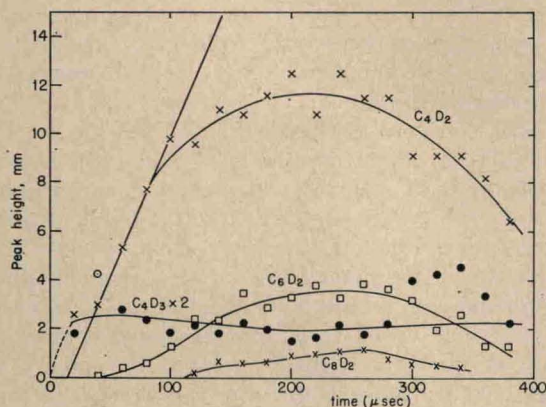


FIG. 4. Formation of intermediates at 2200°K in a 10% mixture of  $C_2D_2$  and neon at  $2.3 \times 10^{-6}$  mole/cc total concentration.

of this the rate constant for the formation of  $C_4H_2$  was calculated from the slopes of straight lines drawn as in Figs. 3 and 4 by the approximate equation

$$d[C_4H_2]/dt = k_a[C_2H_2]^2_{\text{initial}} \quad (a)$$

The results of such calculations are shown in Table II. Experiments at higher and lower temperatures than those of Table II gave qualitatively similar results but were not suitable for rate measurements. In a few experiments the rate constants were calculated from the small fractional decrease in acetylene peak heights by a second-order equation and are thus averages over the entire effective reaction time, about 500  $\mu\text{sec}$ . These constants came out somewhat higher than those in Table II, being close to those of B and K. However, these data are less accurate and are not quantitatively reliable.

Experiments with equimolar mixtures [see Fig. 1(a)] of acetylene and acetylene- $d_2$  revealed isotopic exchange that is about three orders of magnitude faster, as measured by the growth of the acetylene- $d_1$  peak, than the rate of formation of  $C_4H_2$ . Figure 5 shows that the concentration of acetylene- $d_1$  increases as the square of time in the initial stages of reaction. These runs were made at sufficiently low temperatures (1400° to

TABLE I.  $C_4D_2$  and  $C_4D_3$  steady-state concentrations.<sup>a</sup>

$T$ (°K)	$[C_2D_2] \times 10^{-16}$ (molecule/cc)	$C_4D_2$ (mm) Peak height	$C_4D_3$ (mm) Peak height
1682	9.17	0.8	0.5
1770	10.79	2.0	1.1
1873	10.43	2.2	1.0
1926	10.49	7.5	1.2
2002	10.61	6.3	1.2
2011	10.86	7.3	1.4
2016	11.05	8.2	1.2
2021	11.68	7.6	1.2
2140	11.17	16.6	1.4
2145	10.09	15.1	1.6
2190	11.32	12.0	1.2
2195	11.59	12.0	0.8

<sup>a</sup> Runs were made with a mixture containing 7.5-Å  $C_2D_2$  in Ne.

1700°K) that no pyrolysis products were observable during the first 500  $\mu\text{sec}$ . Table III lists rate constants derived from the equation

$$[C_2HD]_t = k_b([C_2H_2] + [C_2D_2])^2 \quad (b)$$

## DISCUSSION

The rate constants of Table II were obtained in that stage of the pyrolysis of acetylene when the rate of formation of diacetylene should substantially equal the loss of acetylene (Figs. 3 and 4). These constants may, therefore, be meaningfully compared with the data of others<sup>1-15</sup> and are indeed found to be between those of Aten and Greene<sup>13</sup> and Kozlov and Knorre,<sup>15</sup> while lower by about a factor of 5 than those of B and K.<sup>14</sup> The present data by themselves do not prove that the rate of disappearance of acetylene is second order. However, when 76 second-order rate constants from 10 publications covering a temperature range from 620° to 2450°K and a wide range of acetylene concentrations are placed on the usual  $\log k$ -vs- $1/T$  plot, the points are seen to show only slight random scatter

TABLE II. Second-order rate constants for diacetylene formation.<sup>a</sup>

$T$ (°K)	Mixture	$[C_2D_2] \times 10^{-15}$ molecule/cc	$k_a \times 10^{15}$ cc/molecule·sec
1903	5.0% $C_2D_2$ in Ne	66.48	2.00
2246	5.0% $C_2D_2$ in Ne	64.80	11.3
2002	7.5% $C_2D_2$ in Ne	106.1	3.26
2016	7.5% $C_2D_2$ in Ne	110.5	2.86
2021	7.5% $C_2D_2$ in Ne	116.8	2.08
2134	7.5% $C_2D_2$ in Ne	109.0	5.97
2140	7.5% $C_2D_2$ in Ne	111.7	5.51
2140	7.5% $C_2D_2$ in Ne	113.2	3.70
2145	7.5% $C_2D_2$ in Ne	100.9	6.75
2195	7.5% $C_2D_2$ in Ne	115.9	4.75

<sup>a</sup> Least-squares equation:

$$\log_{10} k_a = -(10.31 \pm 0.78) - [(38790 \pm 7480)/4.58T],$$

where  $k_a$  is in cubic centimeters per molecule·second.

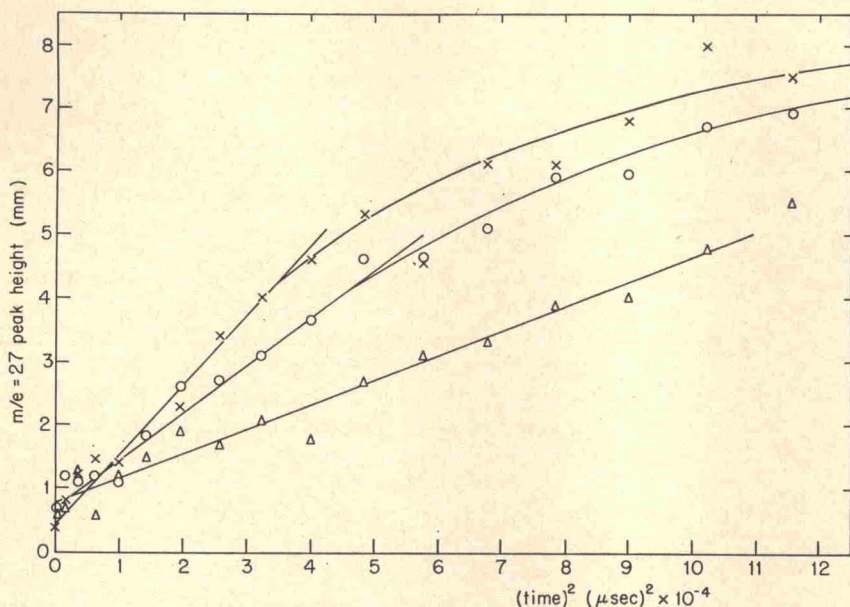


FIG. 5. Concentration of  $C_2HD$  plotted against the square of reaction time in a 5% equimolar mixture of  $C_2H_2 + C_2D_2$  in neon at  $2 \times 10^{16}$  mole/cc total concentration. (X, 1720°; O, 1630°;  $\Delta$ , 1540°K.)

and to lie close to a straight line whose least-squares equation is

$$\log_{10} k = -(10.01 \pm 0.11) - [(41\,610 \pm 620)/4.58T], \quad (c)$$

where  $k$  is in cubic centimeters per molecule·second and uncertainties are standard deviations. Separate least-squares analysis of the upper and lower portions of the very wide temperature range leads to the expressions

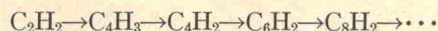
$$\log_{10} k = -(9.80 \pm 0.18) - [(44\,370 \pm 1340)/4.58T](1000^\circ - 2450^\circ K), \quad (d)$$

$$\log_{10} k = -(9.64 \pm 0.29) - [(42\,470 \pm 1040)/4.58T](620^\circ - 1000^\circ K). \quad (e)$$

The similarity of these expressions strongly suggests that essentially the same reaction mechanism is operative over the entire temperature range contrary to the conclusion of Palmer and Dormish<sup>9</sup> who contend that there is a transition at about 1000°K. True enough, the data of some individual investigators give very different activation energies than those of Eqs. (c), (d), and (e); the absolute values of virtually all the rate constants, however, lie close to one Arrhenius plot.<sup>21</sup> The large spread of reported activation energies is but a sad reflection of the difficulties in identifying an activation energy and a pre-exponential rate factor from a limited set of measurements.

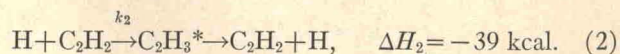
The observations reported here strongly suggest that the pyrolysis of acetylene proceeds through the

<sup>21</sup> The data of B and K are substantially higher than those of other investigations in the same temperature range and we have not included them in the averages.



carbon and hydrogen, and that other products are not important, at least with the present experimental conditions. The isotopic mixing of acetylene, to be considered later, as well as the initial formation of the radical  $C_4H_3$  prove that the mechanism involves radicals and atomic hydrogen. It is interesting to note that all these species have been observed in the acetylene-oxygen flame where the reaction definitely involves radicals.<sup>22</sup> We have considered several complex reaction mechanisms but are unable to identify the correct one because of incompleteness of experimental data. Specifically, no quantitative information could be obtained on atomic and molecular hydrogen and on the radical  $C_2H$  whose ion is obscured by the fragment ion from acetylene. The initial formation of the radical  $C_4H_3$  which attains a readily measurable steady-state concentration and the rapid isotopic exchange of acetylene in accord with the rate law of Eq. (b) are the key new findings. The good fit of the rate data of various investigators to a single Arrhenius-type expression [Eq. (c)] suggests then that essentially the same mechanism is operative over the extremely wide temperature range encompassed by Eq. (c).

The isotopic exchange can be explained by the chain mechanism



<sup>22</sup> U. Bonne, K. H. Homann, and H. G. G. Wagner, Symp. Combust., 10th, Cambridge 1964, 503 (1964).

The heats of reaction given here and in the following have been calculated from the heats of formation given by Bauer *et al.*<sup>23</sup> Since the exchange was observed at

very early stages of the pyrolysis, long before a steady-state concentration of  $C_4H_3$  would have been established at those low temperatures, Eqs. (1) and (2) can be integrated thus:

TABLE III. Rate constants for the reaction  $C_2H_2 + C_2D_2 \rightarrow 2C_2HD$ .<sup>a</sup>

$T$ (°K)	Mixture	$[C_2H_2 + C_2D_2] \times 10^{-16}$ molecule/cc	$k_b \times 10^{28}$ (cc/molecule· sec) <sup>2</sup>
1380	5% ( $C_2H_2 + C_2D_2$ ) in Ne	5.29	3.54
1395	5% ( $C_2H_2 + C_2D_2$ ) in Ne	5.32	2.79
1395	5% ( $C_2H_2 + C_2D_2$ ) in Ne	5.32	3.18
1410	5% ( $C_2H_2 + C_2D_2$ ) in Ne	5.34	5.11
1425	5% ( $C_2H_2 + C_2D_2$ ) in Ne	5.39	4.60
1495	5% ( $C_2H_2 + C_2D_2$ ) in Ne	5.51	10.8
1540	5% ( $C_2H_2 + C_2D_2$ ) in Ne	5.54	9.72
1540	5% ( $C_2H_2 + C_2D_2$ ) in Ne	5.64	6.78
1593	5% ( $C_2H_2 + C_2D_2$ ) in Ne	5.76	8.50
1630	5% ( $C_2H_2 + C_2D_2$ ) in Ne	5.84	15.2
1645	5% ( $C_2H_2 + C_2D_2$ ) in Ne	5.80	22.1
1660	5% ( $C_2H_2 + C_2D_2$ ) in Ne	5.87	24.1
1665	5% ( $C_2H_2 + C_2D_2$ ) in Ne	5.97	20.1
1682	5% ( $C_2H_2 + C_2D_2$ ) in Ne	5.80	27.1
1720	5% ( $C_2H_2 + C_2D_2$ ) in Ne	6.21	20.3
1760	5% ( $C_2H_2 + C_2D_2$ ) in Ne	6.13	24.0
1760	5% ( $C_2H_2 + C_2D_2$ ) in Ne	6.13	28.5
1778	5% ( $C_2H_2 + C_2D_2$ ) in Ne	6.17	34.8
1405	7.5% ( $C_2H_2 + C_2D_2$ ) in Ne	9.01	1.55
1410	7.5% ( $C_2H_2 + C_2D_2$ ) in Ne	8.78	0.93
1440	7.5% ( $C_2H_2 + C_2D_2$ ) in Ne	9.09	2.80
1530	7.5% ( $C_2H_2 + C_2D_2$ ) in Ne	9.43	3.95
1530	7.5% ( $C_2H_2 + C_2D_2$ ) in Ne	9.24	7.32
1550	7.5% ( $C_2H_2 + C_2D_2$ ) in Ne	9.46	5.06
1580	7.5% ( $C_2H_2 + C_2D_2$ ) in Ne	9.65	9.24
1582	7.5% ( $C_2H_2 + C_2D_2$ ) in Ne	9.39	10.8
1722	7.5% ( $C_2H_2 + C_2D_2$ ) in Ne	10.0	14.9
1425	10% ( $C_2H_2 + C_2D_2$ ) in Ne	12.9	2.07
1440	10% ( $C_2H_2 + C_2D_2$ ) in Ne	12.9	2.20
1450	10% ( $C_2H_2 + C_2D_2$ ) in Ne	12.9	2.56
1450	10% ( $C_2H_2 + C_2D_2$ ) in Ne	13.2	2.54
1470	10% ( $C_2H_2 + C_2D_2$ ) in Ne	13.2	2.95
1500	10% ( $C_2H_2 + C_2D_2$ ) in Ne	13.8	2.62
1575	10% ( $C_2H_2 + C_2D_2$ ) in Ne	13.9	5.90
1595	10% ( $C_2H_2 + C_2D_2$ ) in Ne	13.8	10.8
1630	10% ( $C_2H_2 + C_2D_2$ ) in Ne	14.1	7.57
1630	10% ( $C_2H_2 + C_2D_2$ ) in Ne	14.1	8.59
1630	10% ( $C_2H_2 + C_2D_2$ ) in Ne	14.0	8.60
1685	10% ( $C_2H_2 + C_2D_2$ ) in Ne	14.5	9.14

<sup>a</sup> Least-squares equation including all the rate constants:

$$\log_{10} k_b = -(22.53 \pm 0.40) - [(32\,790 \pm 2850)/4.58T],$$

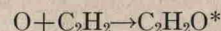
where  $k_b$  is in cubic centimeters squared per molecule squared-second squared.

<sup>23</sup> (a) M. Cowperthwaite and S. H. Bauer, *J. Chem. Phys.* **36**, 1743 (1962); (b) R. E. Duff and S. H. Bauer, *ibid.*, p. 1754.

$$d[H]/dt = k_1[C_2H_2]_0^2; \quad (H)_t = k_1[C_2H_2]_0^2 t, \quad (f)$$

$$d[C_2HD]/dt = k_2[C_2H_2]_0(H)_t; \\ [C_2HD]_t = k_1 k_2 [C_2H_2]_0^3 t^2, \quad (g)$$

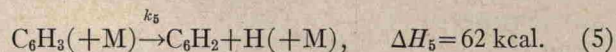
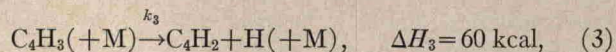
where Subscripts 0 and  $t$  refer to concentrations at times zero and  $t$ , respectively, and for the sake of simplicity in notation, we have neglected to distinguish  $C_2H_2$  and  $C_2D_2$ . The expression in Eq. (g) agrees well with the experimental data of Fig. 5 and Table III. The latter, because of experimental limitation, does not cover a sufficiently wide temperature range to obtain an accurate value of the activation energy, but we have given the least-squares result at the bottom of Table III. If the value for  $k_1$  is taken from Eq. (c), Table III gives for  $k_2$  a range of values between  $10^{-11}$  and  $10^{-12}$  cc/molecule·sec which is in agreement with a previous measurement.<sup>24</sup> Dingle and LeRoy<sup>25</sup> give  $k = 1.34 \times 10^{-14}$  cc molecule<sup>-1</sup>·sec<sup>-1</sup> for the rate of recombination of hydrogen atoms on acetylene. This process must involve the stabilization of the hot radical  $C_2H_3^*$  and hence should have a considerably lower rate constant at the low pressure of the Dingle and LeRoy experiments than  $k_2$ . It is noteworthy that for another exothermic addition of an atom to an acetylene molecule



a rate constant only moderately smaller than  $k_2$  was obtained at room temperature.<sup>26</sup>

An independent identification of  $k_1$  with the  $k$  of Eq. (c) is beset with difficulties because it requires the proof of the complete reaction mechanism which we cannot offer.

Noteworthy are the findings of Table II that the steady-state concentration of  $C_4H_3$  increases very little with temperature, while that of  $C_4H_2$  increases rapidly. We consider this as evidence that the Reaction (1) and the formation of diacetylene ( $2C_2H_2 \rightarrow C_4H_2 + H_2$ ;  $\Delta H = 2.7$  kcal) are not reversible under our experimental conditions and that the sequential pyrolysis  $C_2H_2 \rightarrow C_4H_3 \rightarrow C_4H_2 \rightarrow C_6H_2 \dots$  proceeds in the forward direction only. A partial mechanism that may be considered consists of Reaction (1) and



<sup>24</sup> K. H. Geib and E. W. R. Steacie, *Z. Physik Chem.* **B29**, 215 (1935).

<sup>25</sup> J. R. Dingle and D. J. LeRoy, *J. Chem. Phys.* **18**, 1632 (1950).

<sup>26</sup> C. A. Arrington, W. Brennen, G. P. Glass, J. V. Michael, and H. Niki, *J. Chem. Phys.* **43**, 525, (1965).

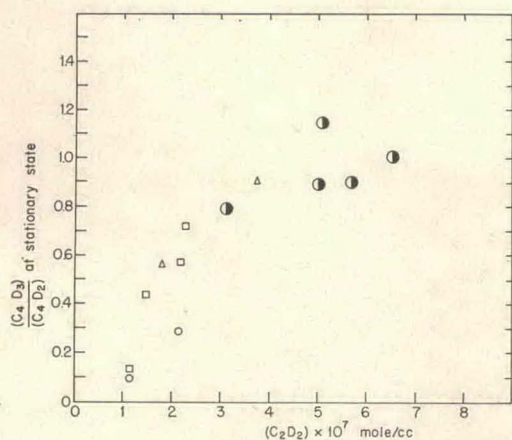


FIG. 6. The ratio of steady-state concentrations of  $C_4D_3$  and  $C_4D_2$  at about 2000°K plotted against the initial concentration of acetylene. Triangles: 7½%  $C_2D_2$  and neon; open circles: 5%  $C_2D_2$  and neon; half-solid circles: 17%  $C_2D_2$  and neon; squares: 5%  $C_2H_2$  and neon.

When the radical  $C_4H_3$  reaches a steady-state concentration, this mechanism gives the rate of formation of diacetylene

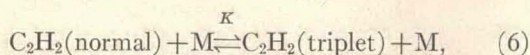
$$d[C_4H_2]/dt = k_3[C_4H_3][M] = k_1[C_2H_2]^2 \quad (h)$$

If the rate of formation of diacetylene by Eq. (h) is identified with the rate of pyrolysis of acetylene [Eq. (c)], the earlier presented calculation of  $k_2$  is justified. At a later stage in the reaction when both  $C_4H_3$  and  $C_4H_2$  reach steady-state concentrations, the mechanism embodying Reactions (1) to (5) leads to the expression:

$$\text{in steady state: } [C_4H_3]/[C_4H_2] = (k_4/k_3)[C_2H_2], \quad (i)$$

which is in agreement with experimental data shown in Fig. 6.

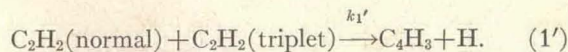
The mechanism, however, aside from not providing for the elimination of hydrogen atoms, presents other serious difficulties. The activation energy of the pyrolytic reaction [Eq. (c)] is in very satisfactory agreement with the heat of Reaction (1) since the reverse reaction should have only a very low activation energy. However, the pre-exponential factor in Eq. (c) is about as large as the collisional frequency, while a steric factor of  $10^{-3}$  would be more reasonable.<sup>27</sup> This may not be a decisive difficulty if, following others,<sup>28</sup> we assume that an "equilibrium" is established:



<sup>27</sup> S. W. Benson, *Foundations of Chemical Kinetics* (McGraw-Hill Book Company, Inc., New York, 1960), p. 280.

<sup>28</sup> See, for example, Ref. 9.

where  $K$  is the equilibrium constant, and Reaction (1) is instead



Then  $k_1 = k_1'/K$  and the larger entropy of the triplet state, if it is not linear,<sup>29</sup> would result in the pre-exponential factor of  $k_1$  being larger than normal.

The triplet state of acetylene is very reactive<sup>30</sup> but for this mechanism to be acceptable the energy of the triplet state must be no higher than 42 kcal<sup>29</sup> and the singlet $\rightleftharpoons$ triplet transition must occur very readily on collisions for the equilibrium to be established rapidly enough. If Reaction (3) has an activation energy of no more than 50 kcal, it can be estimated to be fast enough to account for the observed rate of the establishment of steady state in  $C_4H_3$ . However, the sum  $\Delta H_1 + \Delta H_3 = 106$  kcal is known reasonably accurately<sup>22</sup> and since  $\Delta H_1$  cannot be much larger than 42 kcal, 50 kcal for  $\Delta H_3$  is definitely too low. Furthermore the calculated  $\Delta H_4$  is much too positive to reconcile with the observed rapid increase in the steady-state concentration of diacetylene with temperature. Finally, the mechanism does not dispose of hydrogen atoms. The reaction  $C_2H_2 + H \rightarrow C_2H + H_2$  could be fast enough<sup>23</sup> only if its activation energy is less than about 15 kcal. The mass peak of this radical is unfortunately obscured by that of a fragment ion from acetylene and could not be identified. Further discussion of this and other reactions of hydrogen atoms and free radicals involved would be a pure speculation and seems not justified on the basis of limited experimental data available. However, we wonder whether the mechanism of isotopic exchange between acetylene and deuterium proposed by Kuratani and Bauer<sup>31</sup> is the correct one. In view of our data it could involve the primary formation of hydrogen atoms by Reaction (1), their isotopic exchange with deuterium molecules, and then Reaction (2). However such explanation calls for a different rate law from that reported by Kuratani and Bauer, and we are not able to resolve this difficulty. A free-radical mechanism of the thermal decomposition of acetylene and the nature of the primary reaction we believe, however, to have been established rather firmly.

#### ACKNOWLEDGMENT

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<sup>29</sup> C. K. Ingold and G. W. King, *J. Chem. Soc.* **1953**, 2702.

<sup>30</sup> C. A. Arrington and G. B. Kistiakowsky (to be published).

<sup>31</sup> K. Kuratani and S. H. Bauer, *J. Am. Chem. Soc.* **87**, 150 (1965).