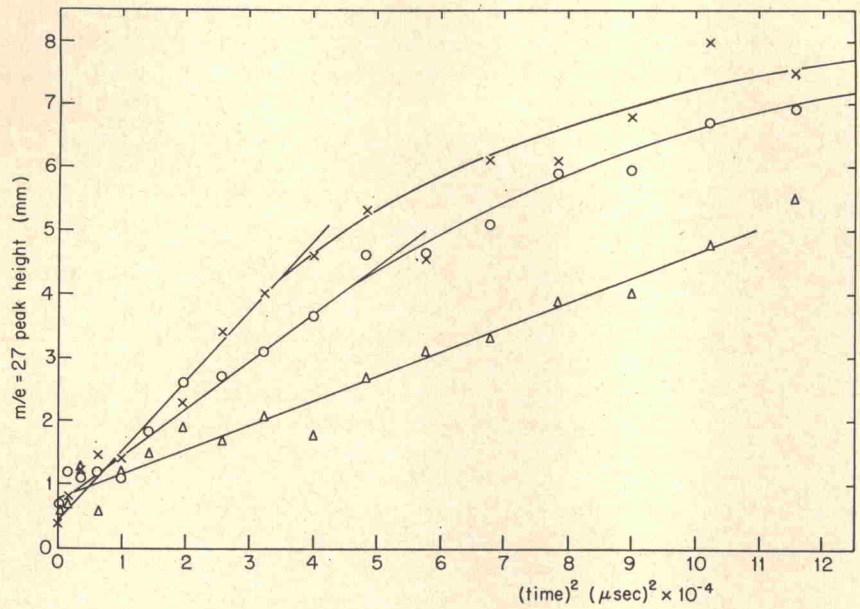

FIG. 5. Concentration of C_2HD plotted against the square of reaction time in a 5% equimolar mixture of $C_2H_2+C_2D_2$ in neon at 2×10^{16} mole/cc total concentration. (×, 1720°; ○, 1630°; △, 1540°K.)

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

$$\log_{10}k=-(10.01\pm0.11)-[(41\,610\pm620)/4.58T], \quad (c)$$

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

$$\log_{10}k=-(9.80\pm0.18)-[(44\,370\pm1340)/4.58T](1000°\text{–}2450°\text{K}), \quad (d)$$

$$\log_{10}k=-(9.64\pm0.29)-[(42\,470\pm1040)/4.58T](620°\text{–}1000°\text{K}). \quad (e)$$

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[9] 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.[21] 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 sequence

$$C_2H_2\rightarrow C_4H_3\rightarrow C_4H_2\rightarrow C_6H_2\rightarrow C_8H_2\rightarrow\cdots$$

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.[22] 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

$$2C_2H_2\xrightarrow{k_1}C_4H_3+H, \qquad \Delta H_1=\ 46\text{ kcal}, \quad (1)$$

$$H+C_2H_2\xrightarrow{k_2}C_2H_3^*\rightarrow C_2H_2+H, \qquad \Delta H_2=-39\text{ kcal}. \quad (2)$$

[21] 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.

[22] 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.*[23] Since the exchange was observed at

TABLE III. Rate constants for the reaction $C_2H_2+C_2D_2\rightarrow 2C_2HD$.[a]

T(°K)	Mixture	$[C_2H_2+C_2D_2]\times10^{-16}$ molecule/cc	$k_b\times10^{23}$ (cc/molecule·sec)^2
1380	5%((C$_2$H$_2$+C$_2$D$_2$) in Ne	5.29	3.54
1395	5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	5.32	2.79
1395	5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	5.32	3.18
1410	5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	5.34	5.11
1425	5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	5.39	4.60
1495	5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	5.51	10.8
1540	5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	5.54	9.72
1540	5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	5.64	6.78
1593	5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	5.76	8.50
1630	5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	5.84	15.2
1645	5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	5.80	22.1
1660	5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	5.87	24.1
1665	5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	5.97	20.1
1682	5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	5.80	27.1
1720	5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	6.21	20.3
1760	5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	6.13	24.0
1760	5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	6.13	28.5
1778	5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	6.17	34.8
1405	7.5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	9.01	1.55
1410	7.5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	8.78	0.93
1440	7.5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	9.09	2.80
1530	7.5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	9.43	3.95
1530	7.5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	9.24	7.32
1550	7.5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	9.46	5.06
1580	7.5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	9.65	9.24
1582	7.5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	9.39	10.8
1722	7.5% (C$_2$H$_2$+C$_2$D$_2$) in Ne	10.0	14.9
1425	10% (C$_2$H$_2$+C$_2$D$_2$) in Ne	12.9	2.07
1440	10% (C$_2$H$_2$+C$_2$D$_2$) in Ne	12.9	2.20
1450	10% (C$_2$H$_2$+C$_2$D$_2$) in Ne	12.9	2.56
1450	10% (C$_2$H$_2$+C$_2$D$_2$) in Ne	13.2	2.54
1470	10% (C$_2$H$_2$+C$_2$D$_2$) in Ne	13.2	2.95
1500	10% (C$_2$H$_2$+C$_2$D$_2$) in Ne	13.8	2.62
1575	10% (C$_2$H$_2$+C$_2$D$_2$) in Ne	13.9	5.90
1595	10% (C$_2$H$_2$+C$_2$D$_2$) in Ne	13.8	10.8
1630	10% (C$_2$H$_2$+C$_2$D$_2$) in Ne	14.1	7.57
1630	10% (C$_2$H$_2$+C$_2$D$_2$) in Ne	14.1	8.59
1630	10% (C$_2$H$_2$+C$_2$D$_2$) in Ne	14.0	8.60
1685	10% (C$_2$H$_2$+C$_2$D$_2$) in Ne	14.5	9.14

[a] Least-squares equation including all the rate constants:

$$\log_{10}k_b=-(22.53\pm0.40)-[(32\,790\pm2850)/4.58T],$$

where k_b is in cubic centimeters squared per molecule squared·second squared.

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

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:

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

$$d[C_2HD]/dt=k_2[C_2H_2]_0(H)_t;$$

$$[C_2HD]_t=k_1k_2[C_2H_2]_0^3t^2, \qquad (g)$$

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.[24] Dingle and LeRoy[25] give $k=1.34\times10^{-14}$ cc molecule^{-1}·sec^{-1} 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

$$O+C_2H_2\rightarrow C_2H_2O^*$$

a rate constant only moderately smaller than k_2 was obtained at room temperature.[26]

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 $C_2H_2\rightarrow C_4H_3\rightarrow C_4H_2\rightarrow C_6H_2\cdots$ proceeds in the forward direction only. A partial mechanism that may be considered consists of Reaction (1) and

$$C_4H_3(+M)\xrightarrow{k_3}C_4H_2+H(+M), \qquad \Delta H_3=60 \text{ kcal}, \qquad (3)$$

$$C_4H_2+C_2H_2\xrightarrow{k_4}C_6H_3+H, \qquad \Delta H_4=44 \text{ kcal}, \qquad (4)$$

$$C_6H_3(+M)\xrightarrow{k_5}C_6H_2+H(+M), \qquad \Delta H_5=62 \text{ kcal}. \qquad (5)$$

[24] K. H. Geib and E. W. R. Steacie, Z. Physik Chem. **B29**, 215 (1935).

[25] J. R. Dingle and D. J. LeRoy, J. Chem. Phys. **18**, 1632 (1950).

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