and C_8H_2. A $C_{10}H_2$ 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 $m/e=51.4\pm0.4$ 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[20] 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 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, 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_4H_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 2.2×10^{-6} mole/cc total concentration.
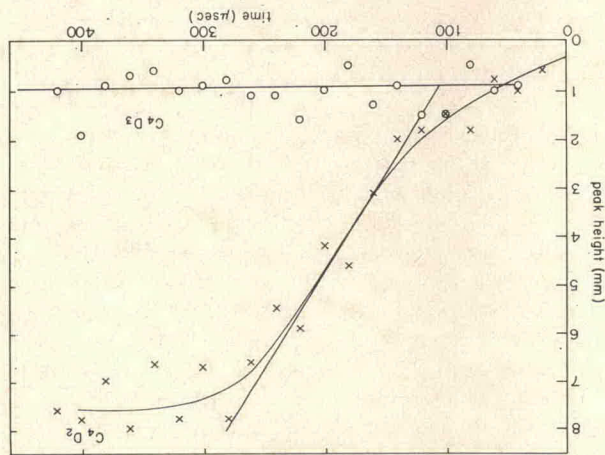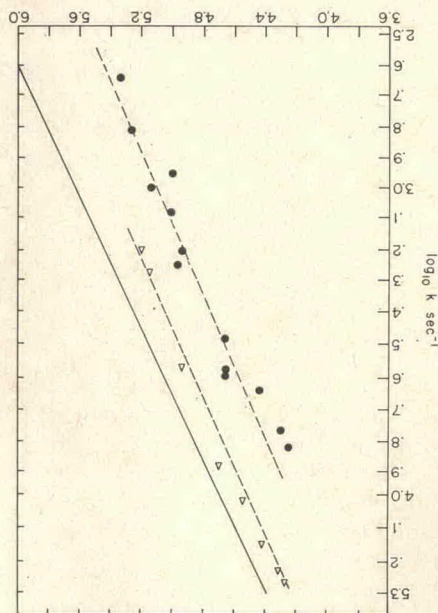
[20] C. E. Melton and W. H. Hamill, J. Chem. Phys. 41, 1469 (1964).

justifies giving considerable credence to quantitative measurements of mass spectra obtained with the T.O.F. mass spectrometer. However, as in earlier work,[17] it was observed that after about 500 μsec 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 μsec, 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,

tion.

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

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
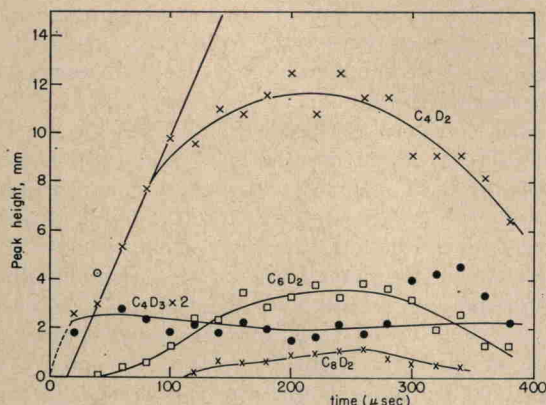

FIG. 4. Formation of intermediates at 2200°K in a 10% mixture of C_2D_2 and neon at 2.3×10^{-6} mole/cc total concentration.

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

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

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 μsec. 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.[a]

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

[a] 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 μsec. Table III lists rate constants derived from the equation

$$[C_2HD]_t = k_b([C_2H_2] + [C_2D_2])^3 t^2. \qquad (b)$$

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[1–15] and are indeed found to be between those of Aten and Greene[13] and Kozlov and Knorre,[15] while lower by about a factor of 5 than those of B and K.[14] 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.[a]

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

[a] Least-squares equation:

$$\log_{10} k_a = -(10.31 \pm 0.78) - [(38\,790 \pm 7480)/4.58T],$$

where k_a is in cubic centimeters per molecule·second.