# 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 μsec, the pyrolysis of acetylene was shown to proceed through the sequence

$$C_2H_2 \rightarrow C_4H_3 \rightarrow C_4H_2 \rightarrow C_6H_2 \rightarrow C_8H_2 \rightarrow \cdots$$
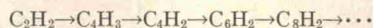
in the temperature range 1600°–2400°K. All these intermediates reach steady-state concentrations, that of the radical C_4H_3 being as large as that of diacetylene under favorable conditions. The primary bimolecular reaction of acetylene in which the radical C_4H_3 is formed must also yield hydrogen atoms. These catalyze an isotopic exchange in mixtures of $C_2H_2 + C_2D_2$ that is about three orders of magnitude faster than the formation of C_4H_2. The initial yield of acetylene-d_1 is given by the expression

$$[C_2HD]_t = k[C_2H_2 + C_2D_2]_0{}^3 t^2,$$

which is consistent with the proposed partial reaction mechanism. The mechanism of conversion of C_4H_3 into C_4H_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.[1-3] Flow reactor techniques were employed to explore the intermediate temperature range,[4-10] while shock waves served to observe the re-

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action at the highest temperatures.[11-15] 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.[14]

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.[3] Vinyl acetylene has been reported in experiments that employ the static, flow reactor, and shock tube techniques. However, Aten and Greene[13] 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)[14] who used a shock tube and a T.O.F. mass spectrometer, but the present work was carried out with vastly improved equipment[16-18] and has led to different conclusions.
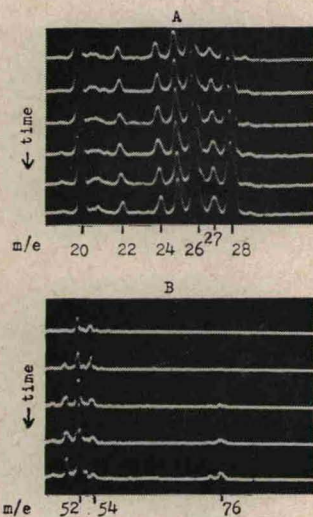

FIG. 1. (A) A few consecutive spectra at intervals of 20 μsec, beginning 120 μsec from reflection of shock showing the formation of C_2HD ($m/e=27$) in an equimolar mixture of C_2H_2 and C_2D_2 in neon at 1425°K; (B) A few consecutive spectra at 2200°K showing the formation of C_4D_3 ($m/e=54$) and slower formation of C_4D_2 ($m/e=52$) and C_6D_2 ($m/e=76$).

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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[16] 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 μsec. 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$=c(m/e)^{\frac{1}{2}}$. 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[17] which connected the shock tube and the T.O.F. was used in all experiments.

RESULTS

To explore further[17] 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

$$N_2O(+Ne) \rightarrow N_2 + O(+Ne).$$
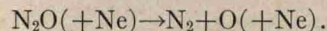
Quite reliable high-temperature data are now available[19] for this reaction. Figure 2 shows the plot of our observed pseudo first-order rate constants and a line which was obtained by Fishburne and Edse at a somewhat higher concentration of N_2O and argon diluent. Since the reaction under these conditions is actually second order, the agreement of our data with those obtained by different techniques is most gratifying and

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