Acetylene Formation from Graphite under Exploding Wire Conditions

By C. W. SPANGLER, S. K. LOTT, and M. J. JONCICH
(*Department of Chemistry, Northern Illinois University, DeKalb, Illinois, U.S.A.*)

REACTIONS of elemental carbon particles have been studied during the past few years under a wide variety of experimental conditions. These studies have ranged from the reactions of recoil ^{11}C, produced by nuclear reaction,[1] to singlet and triplet carbon produced by evaporation from carbon arcs in a high vacuum.[2] Recently, we reported[3] that reaction of graphite with hydrogen under exploding wire conditions produces a mixture of hydrocarbons. In these explosions, which were carried out under a variety of conditions, methane, ethylene, and acetylene were the chief products. Ethane, propane, propylene, and butanes were present as minor products.

Graphite filaments (0·020 in. diameter, 5 in. length) were exploded in a 2 in. diameter cylindrical glass vessel equipped with two gas stopcocks. The explosion apparatus consisted of ten 31·25 microfarad oil-filled capacitors connected in parallel using a copper/polyethylene/Mylar/polyethylene/copper sandwich. The bank was charged to 8 kv, and the energy discharged through the filament by firing a Lovotron switch with a modified Theophanis hydrogen thyratron trigger. The gaseous products were identified by mass spectrometry.

Several possible reaction processes can be envisaged for exploding graphite in a hydrogen atmosphere. Our product analyses indicate that better than 95% of the hydrocarbon yield is methane and C_2 products. Therefore, it is unlikely that carbon aggregates larger than C_2 survive the initial energy surge. The hydrocarbons obtained and their relative amounts are consistent with a methylene intermediate, formed from reaction of monoatomic carbon with molecular hydrogen

$$C + H_2 \rightarrow [CH_2] \qquad (1)$$

$$2[CH_2] \rightarrow CH_2{=}CH_2 \qquad (2)$$

$$[CH_2] + H_2 \rightarrow CH_4 \qquad (3)$$

$$C + CH_2{=}CH_2 \rightarrow HC{\equiv}CH + [CH_2] \qquad (4)$$

An alternative mechanistic pathway would involve intermediates formed by free-radical abstractions:

$$C + H_2 \rightarrow [CH] + H \qquad (5)$$

$$2[CH] \rightarrow HC{\equiv}CH \qquad (6)$$

$$[CH] + H_2 \rightarrow [CH_3] \textit{ etc.} \qquad (7)$$

In an attempt to distinguish between abstraction and combination mechanisms, carbon filaments were exploded in a mixture of hydrogen and deuterium, and the deuterium distribution within the products was determined by mass spectrometry. A revealing observation was an isotope scrambling within the residual hydrogen–deuterium mixture (Table 1).

TABLE 1

	Pre-explosion Composition (% of total)	Residual Composition Explosion I	Explosion II
H_2	51·2	20·4	26·2
D_2	48·8	26·5	24·6
HD	0·03	51·9	48·3

This isotope scrambling indicates that during the process initiated by the explosion, a large percentage of hydrogen and deuterium molecules must be severed. This would not be the case if the major reaction scheme involved direct union of carbon and hydrogen to yield a methylene intermediate.

The isotope distribution in the products is even more revealing. All possible D–H combinations were obtained for acetylene, methane, and ethylene. Since the pathways leading to methane and ethylene are probably more complex, we will, at the present time, consider the mechanism for acetylene formation. The isotope distribution within the acetylene product, observed in two independent explosions, together with that predicted on the basis of initial methyne formation followed by methyne coupling, (and neglecting any possible kinetic isotope effects), is shown in Table 2.

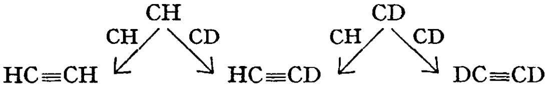
TABLE 2

Product	Explosion I	Explosion II	Predicted
C_2H_2	28	29	26·2
C_2HD	47	46	50·0
C_2D_2	25	25	23·8

The close agreement between the observed and predicted isotope distributions within the acetylene then suggests that it is indeed formed by methyne coupling:

$$C + H_2 \rightarrow CH + H$$

$$C + D_2 \rightarrow CD + D$$



A recent report by Braun, *et al.*,[4] has shown that methyne chemistry can assume major importance in reactions initiated by large, fast energy pulses. Their reactions involved flash photolysis; the duration (5 microseconds) was comparable to exploding wire reactions of carbon (5—10 microseconds).

Further studies are in progress in an attempt to elucidate the probable mechanisms of ethylene and methane formation.

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