The Production of Acetylene by Laser-generated Atomic Carbon

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Summary Thermal carbon atoms, produced by evaporation from graphite with a focussed laser flash, react with hydrocarbons to form acetylene.

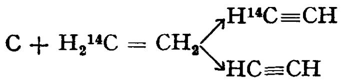
THE chemistry of atomic carbon has been extensively studied by nuclear recoil, photochemical, and thermal methods.[1-3] A major discrepancy emphasized by Skell *et al.*,[4] has been the absence of acetylene—a prominent product in recoil and photochemical systems—in surface deposition experiments. While this discrepancy may be more apparent than real,[6] it is obviously important that it should be resolved.

Thermal methods,[3] in which carbon vapour is produced by volatilisation using arcs, heated rods, and wires *etc.*, may involve reactive molecular species, C_2, C_3, *etc.*, as well as atomic carbon in several low-lying spin states. In gas/solid systems pyrolysis on the hot surface hampers unambiguous interpretation in terms of atomic carbon reactions. Surface deposition experiments[5] avoid this problem, although photolytic effects may still be important. The time-delay technique[4] overcomes these problems, but the results are still ambiguous because of the possibility of complexing between atomic carbon and species in the ambient atmosphere (*e.g.* CO).[6]

The laser experiments described here use thermal C atoms generated under conditions which minimise these difficulties.[7] A Q-switched and focussed laser pulse is used to volatilize carbon from a very small area of graphite. The carbon reacts with the supernatant gas at very low pressures (5—400 microns). Owing to the small dimensions of the hot zone, and the low pressures, both photolysis and pyrolysis of the gas are small. Products are separated by gas chromatography and detected by gas-flow proportional counting or mass spectrometry.

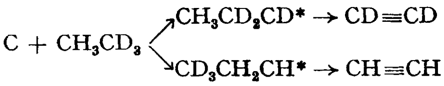
On the whole the reproducibility of the absolute yields was poor, and we are commenting only on the product ratios at this time.

Using ^{14}C labelled graphite and C_2H_4 gas, the major labelled product was acetylene (40—70% of the volatile activity). Large amounts of diacetylene (20—30%) were also observed, although these probably resulted largely from C_2 or higher species. When unlabelled graphite was volatilized into ^{14}C ethylene, acetylene was again the dominant product, and the yield was consistent with the well-known recoil reaction[3] shown in reaction (1).



$$C + H_2{}^{14}C = CH_2 \left\langle \begin{array}{l} \nearrow H^{14}C{\equiv}CH \\ \searrow HC{\equiv}CH \end{array} \right. \qquad (1)$$

Experiments with unlabelled graphite and CH_3CD_3 (with 5% oxygen to reduce interference by radical reactions) yielded acetylenes $C_2H_2:C_2HD:C_2D_2$ in ratios of approximately 1·0:0·4:0·9. (A similar preponderance of C_2H_2 over C_2HD was found using $CH_2{=}CD_2$). These results are consistent with the formation of acetylene following C–H bond insertion [reaction (2)]. Most other mechanisms would yield a preponderance of C_2HD. Since it was not possible to collect methane by-product with our apparatus, it must be admitted that other (although somewhat less likely) mechanisms could also account for these results. The rather high yield of C_2HD does indicate that at least some of the acetylene is being produced by another mechanism. However, further support for the above mechanism was obtained from experiments with unlabelled graphite and a 1:1 mixture of CH_4 and CD_4 (again with 5% O_2). The yield ratios for $C_2H_2:C_2HD:C_2D_2$ were 1·0:0·2:1·1. We consider that this result confirms the route to acetylene by insertion of C atoms into C–H bonds.



$$C + CH_3CD_3 \left\langle \begin{array}{l} \nearrow CH_3CD_2CD^{*} \rightarrow CD{\equiv}CD \\ \searrow CD_3CH_2CH^{*} \rightarrow CH{\equiv}CH \end{array} \right. \qquad (2)$$

A final observation is that the absolute yield of acetylene from methane seemed very much smaller than that from ethylene or ethane. (Although as previously mentioned absolute yields in this work are not precise, this effect is probably real.) Recent recoil and photochemical work[3] has shown that thermalized C atoms do not react efficiently with methane to form acetylene when they are ground state, $C(^3P)$. This suggests that the predominant atomic carbon species formed by thermal means is $C(^3P)$, and that this reacts to form acetylene less efficiently with methane than with higher hydrocarbons.

These results are all consistent with the findings of Skell *et al.* In those experiments reaction occurred with much larger molecules in the solid phase, and under such conditions collisional deactivation would be expected to stabilize the large intermediate formed by carbon insertion before decomposition to acetylene could occur.

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