differences (see 1 and 2 above) indicate that hot atoms are less selective and that the modes of decomposition of their adducts are different from those of atoms of lower energy.

It can be surmised that such hot reactions will only involve a few electron volts of translational energy. Otherwise it seems unlikely that any of the adducts could survive without decomposition.

The lack of temperature dependence in moderated systems (Tables I and II) indicates that there is no appreciable difference in activation energies between the various modes of reaction of thermal carbon atoms with ethylene. This in turn implies that these activation energies are close to zero.

(D) **Conclusions.**—(1) The major mechanism for production of allene is by insertion of a carbon atom into the $\pi$-bond of ethylene. This reaction can occur by the addition of a carbon atom to the $\pi$-bond of ethylene followed by the swift collapse of the resulting cyclopropylidene to allene. (2) A lesser mechanism involves carbon atom insertion into a C–H bond to give the carbene $CH_2{=}CHCH$. This rearranges to allene or methylacetylene more quickly than it adds to ethylene. (3) It is very likely that the great bulk of allene is formed by primary reaction of a singlet ($^1D$) rather than of a triplet ($^3P$) carbon atom. (4) Excess translational energy has qualitatively no effect on the modes by which carbon atoms can react with ethylene. However, hot and thermal carbon atoms produce quantitatively different yield patterns. (5) A substantial fraction of hot carbon atoms, produced in pure ethylene, will react before reaching thermal energies. (6) It is likely that both $\pi$-bond and C–H bond insertion reactions of carbon atoms have very low activation energies.

**Acknowledgments.**—This work was supported in part by the United States Atomic Energy Commission. We wish to thank the director and staff of the Yale University electron accelerator for providing irradiation time and assistance in irradiations. We are grateful to Professor William von E. Doering for encouraging us to do this work and for advice and criticism.

---

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, YALE UNIVERSITY, NEW HAVEN, CONNECTICUT, AND HAVERFORD COLLEGE, HAVERFORD, PENNSYLVANIA]

# Reactions of Carbon Atoms with Ethylene. II. Production of Acetylene and $C_5$ Compounds

BY JAMES DUBRIN,[1a] COLIN MACKAY,[1b] AND RICHARD WOLFGANG

RECEIVED APRIL 30, 1964

Reaction mechanisms of atomic carbon (produced as $C^{11}$ by nuclear transformations) with ethylene have been studied. Sixteen products have been identified, most of them minor. These account for the bulk of the reacting carbon atoms. (Unidentified products appear to be largely polymeric.) Variations of this product spectrum were studied upon change of phase, addition of scavenger, and thermalization of the carbon atoms by neon moderator. These variations suggest that the products fall into two groups of different origin: (1) $C_3$ compounds, allene and methylacetylene; and (2) acetylene and various unsaturated $C_5$ compounds (plus small yields of $C_4$ molecules). The $C_3$ compounds, as discussed in the preceding paper, are believed to be largely formed by insertion of $C(^1D)$ into the C=C and C—H bonds with stabilization of the resulting adducts. However, insertion of $C(^3P)$ into C—H and C=C bonds leads to adducts which are not readily stabilized because of their triplet character. These adducts have sufficient excitation energy to decompose to acetylene, other $C_2$, or $C_3$ species. If decomposition to a stable molecule does not occur prior to collisional energy deactivation, the residual $C_3$ radicals will add ethylene to yield eventually certain specific $C_5$ products. These competitive modes of reaction of the $C_3$ adducts are discussed in detail. It is found that the simple reaction model proposed can fully account for the complex product patterns found.

## Introduction

As has been shown in the preceding paper, the chief products resulting from the reaction of atomic carbon with ethylene fall into two main classes: (1) those compounds having the same composition as the reaction complex, namely, allene and methylacetylene; (2) acetylene and a group of $C_5$ compounds which appear to have a complementary relationship to each other. The preceding paper described in detail the formation of allene and methylacetylene. This report will examine the mechanisms of production of acetylene, the $C_5$, and related compounds.

## Experimental

Both the Yale heavy ion and electron linear accelerators served as sources of $C^{11}$. The detailed methods of production and monitoring of the $C^{11}$ are discussed elsewhere.[2]

Sample containers[2] were filled on a high vacuum line. The gases used, without further purification, were Phillips research grade ethylene, Matheson research grade neon, and Matheson oxygen.

After irradiation (~15 min.), the samples were expanded into four transferring vessels. Analyses were performed by means of gas chromatography using a window flow proportional counter in series with a standard thermistor detector so that mass and activity analyses could be performed simultaneously.[3,4]

Two different columns were used for the analyses of each sample. The total volatile activity of a sample was determined by passing two aliquots directly through the two associated counters. The two additional aliquots were then passed through the two chromatographic columns. The chromatography columns used are listed in Table I.

Identities of all major products were checked on two or more different columns. In addition all reported identifications were confirmed by trapping from the effluent of one column a specific peak with its previously added carrier and injecting it into a second column possessing different characteristics. This procedure confirmed both the purity and identity of the species.

Two types of trapping material placed at the inlet to a counter (or placed between two counters in series) were used to further confirm certain organic bond types. A silver nitrate–glycerin mixture on firebrick was used to trap acetylenic compounds.

(1) (a) Work performed in partial fulfillment of the requirements for the Ph.D. degree at Yale University. (b) Department of Chemistry, Haverford College, Haverford, Pa.

(2) J. Dubrin, C. MacKay, M. Pandow, and R. Wolfgang, *J. Inorg. Nucl. Chem.*, in press.

(3) R. Wolfgang and C. MacKay, *Nucleonics*, **16**, No. 10, 69 (1958).

(4) R. Wolfgang and F. S. Rowland, *Anal. Chem.*, **30**, 903 (1958).

TABLE I

| Column | Temp., °C. | Length, feet | Separations |
|---|---|---|---|
| Activated charcoal | 25 | 5 | CO, $CH_4$, $C_2H_6$ |
| Deactivated alumina | 25 | 30 | CO + $CH_4$, $C_2H_6$, $C_2H_4$, $C_3H_8$, $C_2H_2$, $C_3H_6$ (propylene), $C_3H_6$ (cyclopropane), $C_2H_2$, $C_3H_4$ (allene) |
| Deactivated alumina | 25 | 5 | $C_3H_4$ (allene), $C_3H_4$ (methylacetylene), $C_4H_6$ (methylallene) |
| Ethylene glycol–silver nitrate, mounted on firebrick | 25 | 10 | $C_5H_{10}$ (1-pentene) |
| Dimethylformamide (50%), mounted on firebrick | 0 | 25 | CO + $CH_4$ + $C_2H_6$, $C_2H_4$, $C_3H_8$, $CO_2$, $C_3H_6$ (propylene), $C_3H_6$ (cyclopropane), butenes, butanes |
| Dimethylformamide (25%), mounted on firebrick | 0 | 20 | $C_4H_6$ (ethylacetylene) + $C_5H_8$ (ethylallene), 1-pentyne, 2-pentyne |
| Silicone oil (15% SF-96), mounted on Anakrom ABS | 25 | 60 | General boiling point analysis for $C_4$, $C_5$, and cyclics |
| Hexamethyl phosphoramide (15%), mounted on firebrick | 25 | 5 | $C_2H_2$, $C_3H_4$ (allene), $C_3H_4$ (methylacetylene), $C_4H_6$ (ethylacetylene), $C_5H_8$ (1-pentyne), $C_5H_8$ (ethylallene) |

TABLE II

YIELDS OF IDENTIFIED PRODUCTS IN $C^{11}$–$C_2H_4$ SYSTEM[a]

| System / Product | $C_2H_4$, 76 cm. | $C_2H_4$, 73 cm. $O_2$, 3 cm. | Ne,[b] 76 cm. $C_2H_4$, 4 cm. | $C_2H_4$, liquid (−130°) | $C_2H_4$, solid (−196°) |
|---|---|---|---|---|---|
| Carbon monoxide | 1.2 ± 0.2 | 9.5 ± 0.2 | 4.6 ± 1.0 | 0.5 ± 0.1 | 0.9 ± 0.1 |
| Methane | | <1 | | | |
| Carbon dioxide | <0.1 | 3.1 ± 0.5 | <0.5 | <0.5 | <0.5 |
| Ethane | <0.2 | <0.2 | <0.5 | <0.1 | <0.1 |
| Ethylene | 1.1 ± 0.3 | 2.0 ± 1.0 | <2.0 | 1.7 ± 0.5 | 2.4 ± 0.4 |
| Acetylene | 38.5 ± 3.0 | 35.0 ± 1.5 | 17.5 ± 2.0 | 17.5 ± 2.0 | 19.5 ± 2.0 |
| Propane | <0.1 | <0.1 | <0.5 | <0.7 | <0.8 |
| Propylene | 2.9 ± 0.5 | 2.0 ± 0.5 | 1.0 ± 0.5 | 4.0 ± 0.5 | 4.3 ± 0.5 |
| Cyclopropane | 3.2 ± 0.5 | <0.2 | 1.0 ± 0.5 | 2.2 ± 0.5 | 2.6 ± 0.5 |
| Allene | 16.5 ± 2.0 | 15.5 ± 0.8 | 10.5 ± 2.0 | 11.5 ± 1.5 | 11.2 ± 1.0 |
| Methylacetylene | 4.5 ± 0.5 | 3.7 ± 0.5 | 4.5 ± 1.0 | 4.0 ± 1.0 | 4.0 ± 1.0 |
| 1-Butene | <0.5 | <0.5 | <0.5 | 2.0 ± 0.8 | 1.3 ± 0.5 |
| Butadiene | <0.5 | <0.5 | <0.5 | 2.4 ± 0.8 | 1.6 ± 0.5 |
| Methylallene | <0.5 | <0.5 | 1.0 ± 0.5 | 1.4 ± 0.3 | 2.1 ± 0.3 |
| Ethylacetylene | 0.8 ± 0.4 | <1.0 | 2.7 ± 0.7 | 1.6 ± 0.4 | 1.8 ± 0.4 |
| Vinylacetylene | 10.0 ± 2.0 | 10.0 ± 2.0 | 3.7 ± 0.7 | 2.5 ± 0.4 | 1.0 ± 0.2 |
| 1-Pentene | 1.0 ± 0.3 | <1.0 | <0.7 | 10.0 ± 2.0 | 12.0 ± 2.0 |
| 2-Pentene | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 |
| 1,2-Pentadiene | 3.3 ± 1.2 | <0.2 | 13.5 ± 2.0 | 4.4 ± 0.5 | 6.5 ± 1.5 |
| 1,4-Pentadiene | <0.5 | <0.5 | <1.0 | 3.3 ± 0.4 | 3.0 ± 0.5 |
| 1,3-Pentadiene | <0.2 | <0.2 | <1.0 | <0.5 | <0.5 |
| 2-Methyl-1,3-butadiene | <0.2 | <0.2 | <1.0 | <0.5 | <0.5 |
| 1-Pentyne | 6.6 ± 1.0 | <0.2 | 28.0 ± 4.0 | 6.5 ± 1.5 | 7.5 ± 1.5 |
| 2-Pentyne | <0.2 | <0.2 | <1.0 | <0.5 | <0.5 |
| Vinylcyclopropane | <0.5 | <0.5 | <0.5 | 1.4 ± 0.2 | 3.3 ± 0.4 |
| Cyclopentene | <0.5 | <0.5 | <0.5 | ≤0.5 | ≤0.5 |
| Spiropentane | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |
| Methylenecyclobutane | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 |

[a] Yields are expressed as % total volatile activity. The total volatile activity for ethylene (76 cm.), ethylene plus oxygen, and ethylene plus neon represent 65, 70, and 55%, respectively, of the total expected activity, based on an oxygen monitor.[2] Absolute yields were not determined for condensed state systems. [b] Data of H. E. Rosenberg, of this laboratory, is included.

A mercuric nitrate–mercuric acetate trap[5] was employed to remove all multiply bonded compounds.

## Results

Table II lists the yields of the identified products under various experimental conditions. All yields are reported as a percentage of total volatile activity. These results are the average of at least three or more independent determinations. They are in general agreement with preliminary results reported earlier[6] with the exception of the acetylene yields in the liquid and solid phases, which are significantly lower than the earlier results and now are in agreement with the pattern observed for alkanes.[7]

(5) J. A. Kerr and A. F. Trotman-Dickenson, *Nature*, **182**, 466 (1958).
(6) C. MacKay and R. Wolfgang, *Radiochim. Acta.*, **1**, 42 (1962).
(7) G. Stöcklin and A. P. Wolf, *J. Am. Chem. Soc.*, **85**, 229 (1963); H. Stangl, D. R. Christman, J. B. Cumming, and A. P. Wolf, *J. Phys. Chem.*, **67**, 1735 (1963).

These yields do not represent all the $C^{11}$ which has reacted; certain nonvolatile products were not assayed. By comparing the total volatile activity of a particular ethylene sample with the activity of a standard sample (monitor) of known recovery, its percent total recovery could be determined.[2] These absolute recoveries are listed in Table II; the total recoveries for condensed phase systems were not determined.

## Discussion

This section will attempt to show that the observed product spectrum in the carbon atom–ethylene system, although complex, can be interpreted in terms of a model based on two primary reaction modes of the carbon atom, insertion into the C—H bond and into the C=C bond. Sixteen products have been identified as resulting from the reactions of carbon atoms with ethylene. This complexity is due to

the large number of possible secondary reactions of the initial C + $C_2H_4$ adducts. However, a few of these products account for a major fraction of the total yield and are most relevant to a discussion characterizing the *primary* reaction modes of carbon with ethylene. It is possible to write several mechanisms for the formation of any single product, but the interrelationships between the various products and their diverse dependences on scavenger, moderator, and phase provide a test of the consistency of any given reaction model. A model which appears to be particularly consistent with this data has been constructed on the basis of three assumptions.

**Assumptions.**—(1) The major products result from the reactions of $C(^3P)$ and $C(^1D)$ atoms. The reasons for this assumption are discussed in the accompanying paper.

(2) Both the $C(^3P)$ and $C(^1D)$ atoms add to olefins in two ways, by insertion into the C–H bond and insertion into the carbon–carbon double bond. Both of these modes have been previously postulated.[8-10] There are thus four possible carbon atom–ethylene adducts, $CH_2C^{11}CH_2$ (I) in both singlet and triplet states, and $CH_2CHC^{11}H$ (II) in both singlet and triplet states (see Appendix).

(3) Spin conservation during reaction is assumed. This has the following consequences: (a) Singlet adduct I and II can rupture to molecular or radical fragments but may also be stabilized as either allene or methylacetylene. A reaction mode of much lesser importance is secondary addition to ethylene. (b) Triplet adducts may dispose of their spin and excess energy by bond rupture to give various molecules and radicals (hydrogen atom abstraction by these adducts may under certain conditions also be spin- and energy-permitted modes of reaction). These processes can lead to $C_2$ molecules, $C_2$, and, of course, $C_3$ radicals. The relative importance of these various decomposition modes of the triplet adducts will be primarily determined by their excitation energy and the time available before collisional de-excitation.

The radicals formed in the various fragmentation and spin-disposal modes will tend to add to ethylene in the usual manner expected of free radicals. Hence the triplet adducts not decomposing to stable molecules should *eventually* yield $C_4$, $C_5$, and higher polymeric products.

**Experimental Tests of the Model.**—In addition to the product distribution under standard conditions, four experimental tests of the model are available. A brief description of each is given (also see preceding paper).

(1) **Oxygen Scavenger.**—Low concentrations of oxygen added to ethylene will reduce the yield of any product whose radical precursor shows a significantly higher reactivity toward $O_2$ than toward ethylene. Table II shows that the addition of $O_2$ to ethylene has a negligible effect on the acetylene and vinylacetylene yields, but eliminates the $C_5$ yield.

(2) **Double Tracer Technique.**[11]—By partially labeling the reactant with deuterium and determining the isotopic composition of the $C^{11}$-containing products, the origin of hydrogen atoms in these products can be determined. This makes it possible to establish unambiguously several aspects of the mechanism: whether a given product was formed by interaction of a carbon atom with a single ethylene molecule, or whether radical or abstraction processes are involved in the reaction sequence. Scavenging techniques will not differentiate radical from nonradical processes, if the rates of reaction of the radical with the substrate and with the scavenger are comparable.

(3) **Phase.**—In the condensed state collisional deactivation of excited adducts will be enhanced. This will be reflected by changes in relative yields of various products among gas-, liquid-, and solid-state experiments. The relative yields of acetylene and vinylacetylene are reduced in the condensed states whereas the total $C_5$ yield is increased.

(4) **Neon Addition.**—If a large excess of neon is added to the reactant, the probability that a $C^{11}$ will suffer a high kinetic energy collision with a reactant molecule is greatly reduced. This thermalization of the $C^{11}$ will reduce the probability of hot-atom reactions and will reduce the average energy that the carbon atom can deposit in the primary adduct. In addition neon provides a less efficient medium for de-exciting vibrationally excited species and perhaps electronically excited species as well. The dilution of ethylene with neon causes a sharp reduction in the acetylene and vinylacetylene yields, but enhances the total $C_5$ yield. (For a more extensive discussion of neon as a moderator, see section C of the Discussion of the accompanying paper.)

Figures 1 and 2 summarize possible reaction modes of the initial adducts in accordance with the proposed model. On the basis of these figures qualitative changes in product yields may be understood. Mechanisms for the formation of the individual products will now be discussed in detail.

**Allene and Methylacetylene.**—The production of these $C_3$ products is the subject of the preceding paper.

**Acetylene.**—The proposed model requires that acetylene be formed chiefly by insertion of a triplet carbon atom into the C—H or the C=C bond of ethylene.[8-10]

$$:\dot{C}^{11} + CH_2{=}CH_2 \longrightarrow$$

$$CH_2{=}CH{-}\dot{C}^{11}H \longleftrightarrow \dot{C}H_2{-}\overset{H}{C}{=}\dot{C}^{11}H \quad (1a)$$

$$\dot{C}H_2{-}CH{=}\dot{C}^{11}H \longrightarrow \dot{C}H_2 + HC{\equiv}C^{11}H \quad (1b)$$

$$:\dot{C}^{11} + CH_2{=}CH_2 \longrightarrow \underset{\dot{C}^{11}}{H_2C{-}CH_2} \longrightarrow H_2C{=}\dot{C}^{11}\dot{C}H_2 \quad (2a)^{12}$$

$$CH_2{=}\dot{C}^{11}{-}\dot{C}H_2 \longrightarrow \dot{C}H_2 + \ddot{C}^{11}{=}CH_2 \quad (2b)$$

$$\ddot{C}^{11}{-}CH_2 \longrightarrow HC^{11}{\equiv}CH \quad (2c)$$

Support for this general scheme derives from several sources.

Preliminary results of the double tracer method[13] indicate that approximately 90% of the acetylene derived from the reaction of carbon atoms in an equimolar mixture of $C_2H_4$ and $C_2D_4$ is in the nonisotopically

(8) C. MacKay, M. Pandow, P. Polak, and R. Wolfgang, in "Chemical Effects of Nuclear Transformation," Vol. 11, International Atomic Energy Agency, Vienna, 1961, p. 38

(9) C. MacKay and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2399 (1961).

(10) C. MacKay, P. Polak, H. E. Rosenberg, and R. Wolfgang, *ibid.*, **84**, 308 (1962).

(11) J. Dubrin, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 959 (1964).

(12) The *over-all* enthalpy change for the production of acetylene *via* reactions 1 or 2 is $\sim -30$ kcal. (exoergic). However, reaction 2b is energetically much less favorable than reaction 1b, leading *directly* to acetylene.

(13) J. Dubrin, C. MacKay, and R. Wolfgang, *J. Chem. Phys.*, in press.

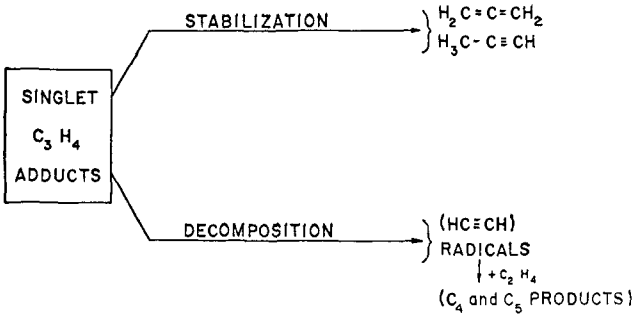



Fig. 1.—Probable reaction modes of adducts formed by addition of C($^1$D) to ethylene. (Minor pathways are indicated by parenthesizing associated products.)

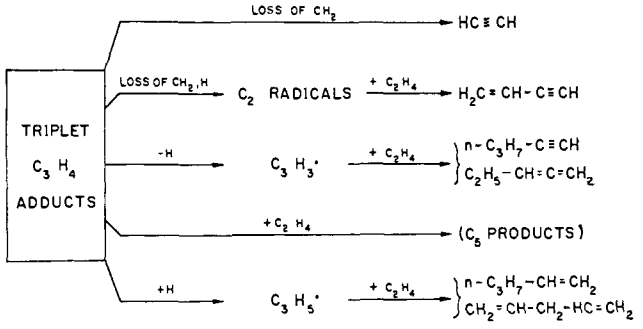



Fig. 2.—Probable reaction modes of adducts formed by addition of C($^3$P) to ethylene. (Minor pathways are indicated by parenthesizing associated products.)

mixed forms of $C_2H_2$ and $C_2D_2$. A similar experiment, using $CH_2{=}CD_2$ as the reactant, indicates that approximately 87% of the acetylene is in the nonmixed forms of $C_2H_2$ and $C_2D_2$. These findings show that most of the acetylene arises from a carbon atom reaction with one methylene group of a single ethylene molecule as shown in (1) and (2).

Thermalization of the C($^3$P), through addition of neon, caused a sharp decrease in the acetylene yield. The adducts formed by thermal carbon atoms will not contain the extra excitation energy deriving from the excess kinetic energy of the carbon. This result suggests that, at low energies, certain modes of decomposition of the adducts to acetylene (such as reaction 2) become relatively less favored. On the other hand, results in neon–ethylene systems indicate that even at infinite moderation where the carbon atom should be completely thermalized acetylene would be formed.[14] This is in accordance with the fact that some possible pathways to this product, specifically reaction 1, are not only exoergic but also involve no highly endoergic steps.

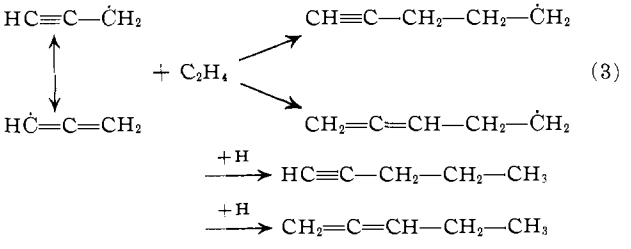
The relative yields of acetylene in liquid and solid are less than in the gaseous (nonmoderated) state. This is reasonable since in the condensed phase enhanced collisional deactivation and the Franck–Rabinovitch cage effect will tend to preserve the integrity of the initial adduct. Addition reactions will therefore be favored over decomposition by C–C bond rupture.

The addition of oxygen has little effect on the acetylene yield. This result is consistent with its postulated formation by a rapid unimolecular fragmentation process.

**Vinylacetylene.**—Vinylacetylene and acetylene have similar dependences on the experimental parameters. This suggests that formation of vinylacetylene is also a consequence of extensive decomposition of the primary adduct to a $C_2$ entity. This species, which could be excited $CCH_2$, $C_2H$, or $C_2$, can then add to an ethylene molecule.

**$C_5$ Condensation Products.**—A reasonable route for the production of the $C_5$ compounds involves the addition of three-carbon-atom radicals or diradicals to ethylene. As discussed earlier, neon moderation or the effective de-excitation provided by the solvent cage in condensed phase relative to the gas phase should enhance the yields of three-carbon radicals.[15] The increase in the yield of $C_5$ products under these conditions is thus reasonable. Furthermore, the elimination of these products with $O_2$ scavenger is consistent with the assumption of a radical intermediate.

The triplet $C_3H_4$ might add directly. Alternatively, it contains enough energy to decompose to $C_3H_3\cdot$ by hydrogen elimination. This process would be especially important in highly moderated systems since collisional removal of excitation energy will be inefficient in neon. It is therefore not surprising to find that the *two* products expected as a result of $C_3H_3\cdot$ addition, 1-pentyne and ethylallene (reaction 3), are found in very high yields in the moderated system.[16]




(3)

In condensed phase the importance of decomposition modes is reduced. $C_3H_4$ triplets and a further intermediate formed from them by hydrogen abstraction, $C_3H_5$ (allyl radical), should be expected to play more important roles.[17]

There is some evidence for allyl radicals as intermediates in our system (condensed state). Allyl radicals are known to add to ethylene in the gas phase to yield 1,4-pentadiene.[18] We observed both this product and 1-pentene in high yield in the reaction of carbon

(14) H. E. Rosenberg, this laboratory, unpublished results.

(15) The increase in yield of 1-pentyne and ethylallene at the expense of acetylene can be understood in terms of the following reactions, which are listed in order of decreasing energy requirements (reactions c and d have very similar energy requirements).

$$CH_2C^{11}CH_2\ (I) \longrightarrow CH_2 + C^{11}CH_2 \qquad (a)$$

$$CH_2C^{11}CH_2\ (I) \longrightarrow CH_2C^{11}CH + H \qquad (b)$$

$$CH_2CHC^{11}H\ (II) \longrightarrow CH_2CC^{11}H + H \qquad (c)$$

$$CH_2CHC^{11}H\ (II) \longrightarrow CH_2 + HC{\equiv}C^{11}H \qquad (d)$$

A lower energy carbon atom would favor reaction b relative to a. Furthermore, if, as indicated in the preceding paper, a thermal carbon atom is more selective, it should favor formation of the double bond adduct 1, which reacts by either (a) or (b). The net results of these two effects is to increase the total amount of reaction b, leading eventually to $C_5$ products, and decrease (d), leading to acetylene.

(16) This hypothesis is consistent with the properties of the $C_3H_3$ radical as observed by R. Srinivasan, *J. Am. Chem. Soc.*, **82**, 5063 (1960), J. Collin and F. P. Lossing, *Can. J. Chem.*, **35**, 778 (1957), and P. Kebarle, *J. Chem. Phys.*, **39**, 2218 (1963). Their work indicates that the addition modes of the $C_3H_3$ radical are energy dependent. Low energy $C_3H_3$ radicals react as if they had the $CH{\equiv}C{-}\dot{C}H_2$ structure, while higher energy $C_3H_3$ radicals show reactions characteristic of both the $CH{\equiv}C{-}\dot{C}H_2$ and $CH_2{=}C{=}\dot{C}H$ structures. The addition of these higher energy radicals to ethylene would then be expected to lead to 1-pentyne and ethylallene as observed.

(17) It is also possible that insertion of CH into $C_2H_4$ accounts for a part of the allyl radical formation.

(18) W. A. Bryce and D. J. Ruzicka, *Can. J. Chem.*, **38**, 835 (1960).

with condensed ethylene.[19,20] These reactions are shown below.

$$\mathrm{CH_2{=}CH{-}\dot{C}H_2 + C_2H_4 \longrightarrow CH_2{=}CH{-}CH_2{-}CH_2{-}\dot{C}H_2}$$

$$\mathrm{CH_2{=}CH{-}CH_2{-}CH_2{-}\dot{C}H_2} \xrightarrow{+H} \mathrm{CH_2{=}CH{-}CH_2{-}CH_2{-}CH_3} \qquad (4)$$

$$\mathrm{CH_2{=}CH{-}CH_2{-}CH_2{-}\dot{C}H_2} \xrightarrow{-H} \mathrm{CH_2{=}CH{-}CH_2{-}CH{=}CH_2}$$

The direct addition of $C_3H_4$ triplet to ethylene would also account for all the products which we have observed (reactions 5 and 6). However, it would then

$$\mathrm{CH_2{=}\dot{C}^{11}{-}\dot{C}H_2 + C_2H_4 \longrightarrow CH_2{=}\dot{C}^{11}{-}CH_2{-}CH_2{-}\dot{C}H_2} \qquad (5)$$

$$\mathrm{CH_2{=}\dot{C}^{11}{-}CH_2{-}CH_2{-}\dot{C}H_2} \xrightarrow[\text{shift}]{1\text{-}5} \mathrm{CH{\equiv}C^{11}{-}CH_2{-}CH_2{-}CH_3}$$

$$\mathrm{CH_2{=}\dot{C}^{11}{-}CH_2{-}CH_2{-}\dot{C}H_2} \xrightarrow[\text{shift}]{3\text{-}5} \mathrm{CH_2{=}C^{11}{=}CH{-}CH_2{-}CH_3}$$

$$\mathrm{CH_2{=}\dot{C}^{11}{-}CH_2{-}CH_2{-}\dot{C}H_2} \xrightarrow[\text{shift}]{4\text{-}2} \mathrm{CH_2{=}C^{11}HCH_2{-}CH{=}CH_2}$$

$$\mathrm{CH_2{=}CH{-}\dot{C}^{11}H \leftrightarrow CH_2{-}CH{=}\dot{C}^{11}H + C_2H_4 \longrightarrow \dot{C}H_2{-}CH{=}C^{11}H{-}CH_2{-}\dot{C}H_2} \qquad (6a)$$

$$\mathrm{CH_2CH{=}C^{11}HCH_2\dot{C}H_2} \xrightarrow[\text{shift}]{4\text{-}1} \mathrm{CH_3{-}CH{=}C^{11}H{-}CH{=}CH}$$

$$\mathrm{CH_2CH{=}C^{11}HCH_2\dot{C}H_2} \xrightarrow[\text{shift}]{2\text{-}5} \mathrm{CH_2{=}C{=}C^{11}H{-}CH_2{-}CH_3}$$

$$\mathrm{C^{11}H{=}CH{-}\dot{C}H_2 + C_2H_4 \longrightarrow \dot{C}^{11}H{=}CH{-}CH_2{-}CH_2{-}\dot{C}H_2} \qquad (6b)$$

$$\mathrm{C^{11}H{=}CHCH_2CH_2\dot{C}H_2} \xrightarrow[\text{shift}]{2\text{-}5} \mathrm{C^{11}H{\equiv}C{-}CH_2{-}CH_2{-}CH_3}$$

$$\mathrm{C^{11}H{=}CHCH_2CH_2\dot{C}H_2} \xrightarrow[\text{shift}]{4\text{-}1} \mathrm{C^{11}H_2{=}CH{-}CH_2{-}CH{=}CH_2}$$

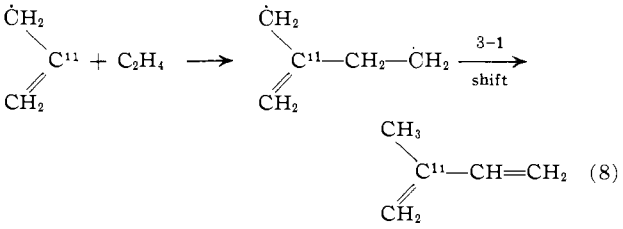
seem reasonable to expect further products which are not observed, particularly 1,3-pentadiene[23] and 2-methyl-1,3-butadiene (reactions 7 and 8). The failure

$$\mathrm{CH_2{=}CH{-}\dot{C}^{11}H \leftrightarrow \dot{C}H_2{-}CH{=}\dot{C}^{11}H + C_2H_4 \longrightarrow}$$

$$\mathrm{CH_2{=}CH{-}\dot{C}^{11}H{-}CH_2{-}\dot{C}H_2} \xrightarrow[\text{or 4-1 shift}]{4\text{-}5} \qquad (7)$$

$$\mathrm{\dot{C}H_2{-}CH{=}C^{11}H{-}CH_2{-}\dot{C}H_2} \xrightarrow[\text{shift}]{3\text{-}5 \text{ or } 2\text{-}5}$$

$$\mathrm{CH_2{=}CH{-}C^{11}H{=}CH{-}CH_3}$$
$$\mathrm{CH_2{=}C{=}C^{11}H{-}CH_2{-}CH_3}$$



(8)

to observe these products in significant yield indicates that in condensed phase as in the neon–ethylene experiments this mechanism is not as consistent with the experimental observations as that involving $C_3H_3\cdot$ and allyl radical addition to ethylene.[24]

Thus, on the basis of the three assumptions previously introduced, and in particular on the assumption of C—H and C=C insertion by the carbon atom, it is possible to construct a plausible mechanism which not only can account for the observed $C_5$ product spectrum but also can account for the absence of certain significant products and, furthermore, is consistent with the variation in product spectrum with variation in experimental parameters.

**Other Products.**—Mechanisms for production of certain minor products, such as $C_4$ compounds other than vinylacetylene, have not been specifically discussed, but are readily shown to be consistent with the postulated model. The only products not falling within the scope of this model are cyclopropane and propylene which are produced in about 6% yield in gas and condensed phases. The formation of these products by insertion of $CH_2$ into ethylene has been discussed elsewhere.[8-10] (See also footnote 20.) Their appearance supports the original hypothesis that a small but significant fraction of carbon atoms reacts with hydrocarbons to form $CH_2$.[7,27]

## Summary

These results are in full accord with the following model of carbon atom reactions: (1) Both $C(^3P)$ and

(19) Cyclopentene is also formed by the reaction of allyl radicals with ethylene in the gas phase at 20 cm. pressure. We do not observe this, but do find a significant yield of 1-pentene. It is possible that in condensed phase the intermolecular hydrogen abstraction reaction to form 1-pentene predominates over the intramolecular cyclization reaction, and that the reverse is true in the gas phase, but we know of no independent evidence on this point. In any event the excitation energy of allyl radicals formed in these systems should be different from that of allyl radicals formed in other ways, and thus a difference in product pattern is not unreasonable.

(20) Addition of a hydrogen atom to the allyl radical might also contribute to the propylene yield in the condensed phase.[18] Previously this product has been completely attributed to $CH_2$ addition to ethylene, as has the yield of cyclopropane.[8,10] However, when formed by this mechanism, the ratio of the yields of cyclopropane to propylene is known to increase with pressure[21] and should also increase on going to condensed phase. In agreement with this, it has been shown that in nitrogen matrices at 20°K. cyclopropane is the major yield[22] while the reverse is true in the gas phase.[21] However, we find a *decrease* in this ratio on going from gas to condensed phases, suggesting a contribution to the propylene yield in condensed phase by a mechanism which cannot lead to cyclopropane.

(21) H. M. Frey and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **79**, 6373 (1957).

(22) W. B. DeMore, H. O. Pritchard, and N. Davidson, *ibid.*, **81**, 5784 (1959).

(23) The failure to find 1,3-pentadiene is particularly significant. There is good reason to expect this as a product of the reaction of the triplet species $\dot{C}^{11}H{-}CH{=}CH_2 \rightarrow \dot{C}^{11}H{-}CH{-}\dot{C}H_2$ with ethylene. One electron is effectively localized on the CH group. Addition to ethylene using this localized electron preserves the delocalized character of the second electron. Therefore this mode should be energetically favored over addition modes using the delocalized electron. It is possible that the proposed radical precursor to pentadiene, $CH_2{=}CH{-}\dot{C}H{-}CH_2{-}\dot{C}H$, may decompose to butadiene and triplet (ground-state) $CH_2$, a favored mode. Thus the butadiene yield may set an upper limit on the importance of direct addition of triplet $C_3H_4$ to ethylene.

(24) Additional evidence indicating lesser importance for the mechanism involving direct addition of triplet species to ethylene is the failure to find cyclic $C_5$ products (Table II). The formation of cyclic products seems to be one of the best established reactions of triplets with olefins in both condensed[25] and gas phases.[26] However, the relative importance of this mode of reaction is not completely clear.[24] We have sought such products in this system and have found only vinylcyclopropane in low yield, and this product can be accounted for by the addition of a singlet $C_3$ carbene to ethylene. (See accompanying paper.) This result of course does not rule out triplet addition reactions since our conditions are quite different from those of other workers. For example, concentrations of triplet species in this work are at most $10^{-12}$ that of ethylene, effectively ruling out all possibility of triplet–triplet reactions. Furthermore, the use of $C^{11}$ tracer techniques allows us to work at concentrations of other radicals at least 100 times lower than is customary in radical studies, thus greatly reducing the importance of triplet-radical reactions.

(25) G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963).

(26) J. P. Chesick, *J. Am. Chem. Soc.*, **85**, 3718 (1963).

(27) A. P. Wolf, *Advan. Phys. Org. Chem.*, in press.

$C(^1D)$ atoms are available for reaction. (2) Both types of atoms insert into both the C=C and C—H bonds to yield four possible adducts. (3) The singlet adducts formed by $C(^1D)$ insertion may be stabilized to give allene and methylacetylene (as discussed in detail in the preceding paper). If they are not stabilized they will decompose to molecules or radicals. (4) The adducts formed by $C(^3P)$ insertion are, because of their triplet nature, not readily stabilized. They contain sufficient excitation energy to permit decomposition to acetylene (a major product), to $C_3$ radicals (which can add to ethylene to give $C_5$ compounds), and, less often, to $C_2$ fragments (which can then add to ethylene to give small yields of $C_4$ molecules). (5) Any triplet $C_3$ adducts which do not decompose by C–C or C–H bond rupture can eventually be incorporated into $C_5$ compounds through reactions involving ethylene. (6) Approximately 6% of the $C^{11}$ atoms reacts to form $C^{11}H_2$.

**Acknowledgments.**—The assistance of Maryan Marshall in sample analyses was most helpful. We are particularly grateful to the directors and staffs of the Yale heavy ion and electron accelerators for providing irradiation facilities. These studies were supported by the U. S. Atomic Energy Commission.

## Appendix

**Relative Importance of C and CH in the Ethylene System.**—In this discussion and in the preceding paper it is implicitly assumed that most products derive from the reactions of adducts formed by direct carbon atom addition. However, if CH is formed by initial reaction of C with the substrate, this intermediate may form adducts similar to those formed by direct addition of C. The possible role of CH in reactions with alkanes has been discussed,[8,9,28] although no definite conclusions have been reached. The addition of CH to ethylene must then also be considered as an alternate route to some products.[10] At this stage the postulate of direct carbon atom addition to ethylene provides a more plausible explanation of the formation of most products. The reasons for this preference are listed below, in connection with several major products.

(1) **Acetylene.**—In double tracer experiments using equimolar mixtures of $C_2H_4$ and $C_2D_4$, approximately 90% of the acetylene formed occurs as $C_2H$ and $C_2D_2$.[13] If acetylene primarily resulted from a CH reaction more mixing (to form $C_2HD$) would be expected.

(2) **Allene.**—From an equimolar mixture of $C_2H_4$ and $C_2D_4$ more than 87% of the allene formed occurs as $C_3H_4$ and $C_3D_4$. (See accompanying paper, ref. 6.) The absence of extensive mixing here strongly suggests a direct carbon atom reaction. However, the following reaction of CD to give allene ($C_3H_4$) cannot be rigorously excluded.

$$CD + CH_2{=}CH_2 \longrightarrow CH_2{=}CD{-}CH_2{}^* \longrightarrow CH_2{=}C{=}CH_2 + D$$

Rupture of the C–D bond of the excited allyl radical is a favored decomposition mode and has been observed.

However, a major role for allyl radicals in allene formation seems unlikely from the following results: (a) The allyl radical is particularly stable and at atmospheric pressure some allyl radicals should be stabilized by collisional deactivation, yet none of the products of allyl radical addition to ethylene (cyclopentene and 1,4-pentadiene) are observed in the gas phase. (b) In condensed phase, products characteristic of the reaction of allyl radicals are found in high yield (~19%). However, experimentally there seems to be no relationship between these and allene.[29] On going from gas to condensed phase, the allyl radical yield goes from 0 to 19%, while the allene yield only decreases from 16.5 to 11.5% (furthermore, part of this latter decrease is accounted for by the formation of vinylcyclopropane).

(3) **$C_5$ Products.**—In both gas and condensed phase 1-pentyne and ethylallene have been found. These products are not among those known to arise from the reaction of allyl radicals with ethylene, and indeed it seems unreasonable that they should arise from this source (or from other possible $C_3H_5$ radicals such as $CH_3{-}\dot{C}{=}CH_2$). On the other hand they fit into the proposed carbon atom reaction model discussed in this paper.

We have shown above that a mechanism involving CH cannot account for the major yield of acetylene, and that it is not the most plausible source of other products. Nevertheless, although completely convincing evidence is lacking at present, it is quite likely that some CH is formed and that it does account for part of the yield of some products. However, the very difficulty of distinguishing between C and CH reactions implies that where CH is involved it reacts by mechanisms very similar to those proposed for C.

(28) (a) A. P. Wolf and G. Stocklin, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan., 1964, p. 32C; (b) E. P. Rack, C. E. Lang, and A. F. Voigt, *J. Chem. Phys.*, **38**, 1211 (1963).

(29) This statement is based on the reasonable assumption that the total yield of volatile products in condensed phase is not appreciably lower than in the gas phase.