PHYSICAL AND INORGANIC CHEMISTRY

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

The Reactions of Atomic Carbon with Ethylene.   I.   Production of Allene and Methylacetylene

BY MARYAN MARSHALL,[1a] COLIN MACKAY,[1b] AND RICHARD WOLFGANG

RECEIVED APRIL 30, 1964

Insertion reactions of carbon-11 atoms into ethylene have been further investigated by detailed studies on two important products: C^{11}-allene and C^{11}-methylacetylene. The carbon-11 atoms were produced as hot atoms by nuclear techniques. Degradative studies show that most of the allene is center labeled ($CH_2=C^{11}=CH_2$) under all conditions. End labeling is more important in methylacetylene than it is in allene. These data, results of double tracer experiments and observations on phase, temperature, and moderator dependences, indicate that most of the allene and a significant fraction of the methylacetylene are formed by carbon atom insertion into the ethylene π-bond. Insertion into the C–H bond, giving end-labeled allene and methylacetylene, is of lesser importance. The principal species involved in the predominant center-labeling mode seems to be the $C(^1D)$ rather than the ground state $C(^3P)$ atom. Moderators were used to distinguish between reactions at thermal and high kinetic energies. It was found that both hot and thermal carbon atoms reacted by similar modes, but that the thermal species showed more discrimination, favoring π-bond over C–H bond attack. No temperature effect was found in the moderated system, in keeping with the expectation that both types of insertion reactions have very low activation energies.

Introduction

Two insertion reactions have been postulated to be important in the reaction of atomic carbon with hydrocarbons: insertion into C—H and into C=C double or π bonds.[2-4] In this and the accompanying paper, these mechanisms are examined in detail using ethylene as the prototype system.

Allene is the second largest product from the reaction of carbon atoms with ethylene under most conditions. It is of particular interest because it, and its isomer, methylacetylene, have the composition of the original reaction complex, indicating that the reaction paths by which they were formed may be particularly simple. Furthermore, the origins of these two products may be conveniently studied by several complementary techniques: (1) yield dependence as a function of phase, temperature, and moderator; (2) degradative techniques, serving to place the position of the reacting carbon atom in the final product (preliminary results of such a study have been reported in an earlier communication[5]); (3) double tracer techniques, serving to trace the origin of the hydrogen atoms in the final product.[6]

(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) C. MacKay, P. Polak, H. E. Rosenberg, and R. Wolfgang, J. Am. Chem. Soc., **84**, 308 (1962).

(3) C. MacKay and R. Wolfgang, ibid., **83**, 2399 (1961).

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

(5) M. Marshall, C. MacKay, and R. Wolfgang, Tetrahedron Letters, No. **29**, 2033 (1963).

(6) J. Dubrin, C. MacKay, and R. Wolfgang, J. Am. Chem. Soc., **86**, 959 (1964).

Results from all of these studies are here combined to give what is hoped to be a reasonably unambiguous picture of allene formation. What is learned from allene then serves to provide an over-all model of the reactions of carbon atoms with ethylene, and hydrocarbons in general.

Outline of Technique.—Atomic carbon (20.4-min. half-life) is produced by nuclear reaction. In most experiments only $\sim 10^8$ atoms are produced. These atoms are formed at high kinetic energy within the ethylene and lose energy by collision until they react to become combined. The trace quantities of products containing C^{11} are separated by gas chromatography and assayed. A given product may be degraded provided that such degradation and assay is completed within a few half-lives.

The nucleogenic mode of production of carbon as initially hot atoms raises several questions. (1) What are the probable charge and excitation states of the carbon as it reacts? This is discussed in the following section. (2) Do the carbon atoms react while they have excess kinetic energy or after thermalization? Are their hot and thermal reactions appreciably different? These questions are taken up in the Discussion.

Charge and Excitation State of Reacting Carbon Atom.—A carbon atom formed by the $C^{12}(\gamma,n)C^{11}$ reaction using a 40-Mev. Bremsstrahlung beam is probably produced as an ion.[7] However, such ions are produced at sufficiently high energies ($\sim 10^6$ e.v.), so

(7) S. Wexler, to be published in "Actions Chemiques et Biologiques des Radiations," Vol. VIII, M. Haissinsky, Ed., Mason and Cie, Paris.

that their charge state when they reach the much lower energies ($\gtrsim 10$ e.v.) where they may combine chemically is determined by a very large number of intervening charge-changing collisions. This has been discussed previously for the analogous case of recoil tritium.[8]

The charge state of the reacting carbon atom is determined by the energies at which the cross sections for the various charge-transfer processes have their maxima. These maxima are quite high, and, in general, are higher the lower the energy at which they occur.[9,10] Thus, the predominant charge state of the reacting atom should be determined by the lowest energy process.

The approximate energies at which the cross-section maxima for the charge-transfer reactions occur may be calculated using the resonance rule.[10] This rule states that the maximum cross section for a process in which there is an energy change, ΔE, will occur when $v_{max} = [a|\Delta E|]/h$, where h is Planck's constant, a is an interaction distance, $\sim 7 \times 10^{-8}$ cm.,[9] and v_{max} is the relative velocity of the interacting particles at the energy of maximum cross section. The predictions of the rule for various charge-transfer processes are summarized in Table I.

TABLE I
APPLICATION OF THE RESONANCE RULE TO CARBON

		—M = C_2H_4—		—M = O_2—	
		ΔE,[b] e.v.	E_{max},[c] e.v.	ΔE,[b] e.v.	E_{max},[c] e.v.
(1)	$C(^3P) + M \rightarrow C^- + M + e^-$	11.3	2×10^5	11.3	2×10^5
(2)	$C(^1D) + M \rightarrow C^+ + M + e^-$	10.1	1.6×10^5	10.1	1.6×10^5
(3)	$C^+ + M \rightarrow C(^3P) + M^+$	0.8	1×10^3	0.9	1.4×10^3
(4)	$C^- + M \rightarrow C(^1D) + M^-$	0.4	3×10^2	2.1	7×10^3
(5)[d]	$C(^3P) + M \rightleftarrows C(^1D) + M$	1.2	2×10^3	1.2	2×10^3
(6)	$C(^1D) + M \rightarrow C(^1D) + M^{*a}$	5.8	5.4×10^4	2.3	9.5×10^3
(7)	$C(^1D) + M \rightarrow C(^3P) + M^{*a}$	3.4	1.8×10^4	0.3	1.4×10^2

[a] M* denotes lowest-lying excited state. [b] Ionization potentials: $C(^3P)$ 11.3 e.v.[e]; $C(^1D)$ 10.1 e.v.[f]; C_2H_4 10.5 e.v.[e]; C_2H_4 (triplet) 5.9 e.v.[g]; O_2 12.2 e.v.[e]; O_2 (singlet) 11.1 e.v.[h] [c] $E_{max} = 0.5m[(\Delta E|a)/n]^2 = 1600(\Delta E)^2$ e.v. for C^{11} if $a = 7 \times 10^{-8}$ cm. [d] Spin forbidden reaction; will have low cross section. [e] R. W. Kiser, "Tables of Ionization Potentials," United States Atomic Energy Commission, Office of Technical Information, June 20, 1960. [f] $C(^3P) \rightarrow C(^1D)$, 1.2 e.v., G. Herzberg, "Atomic Spectra and Atomic Structure," Dover Publications, New York, N. Y., 1944). [g] $C_2H_4 \rightarrow C_2H_4(T)$, 4.6 e.v. [R. S. Mulliken, J. Chem. Phys., 33, 1596 (1960)]. [h] $O_2 \rightarrow O_2(S)$, 0.98 e.v. [G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950.

From Table I, reactions 1 and 2, it can be seen that the cross sections for ionization of atomic carbon decrease below about 10^5 e.v. The cross sections for neutralization of carbon, reactions 3 and 4, increase up to $\sim10^2$–10^3 e.v. Since the neutral atom formed cannot re-ionize at or below 10^3 e.v., the chemically reacting species is expected to be a neutral carbon atom.

The excitation state of the carbon atom may similarly be considered using this rule. Such a treatment indicates that no highly excited electronic state should be important. Only relatively low-lying states such as the $C(^3P)$, $C(^1D)$, and $C(^1S)$ would be expected to survive to the chemical energy range.

(8) M. F. A. El-Sayed, P. Estrup, and R. Wolfgang, J. Phys. Chem., 62, 1356 (1958).

(9) J. B. Hasted, in "Atomic and Molecular Processes," D.R. Bates, Ed., Academic Press, Inc., New York, N. Y., 1962, p. 696.

(10) H. S. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, London, 1952.

Experimental

General Method.—An ethylene sample was irradiated with a 40-Mev. Bremsstrahlung beam to produce $\sim10^8$ atoms of C^{11} from the $C^{12}(\gamma,n)C^{11}$ reaction. The C^{11}-allene or C^{11}-methylacetylene was separated and assayed by gas chromatography using methods described elsewhere.[11,12] The separated product was converted to C^{11}-acetone by acidic hydrolysis and 1,3-C^{14}-acetone was added to facilitate determination of the yields of subsequent steps. The iodoform reaction was performed on the acetone. The iodoform and acetic acid were separated and purified. Acetone, iodoform, and acetic acid fractions were counted for C^{11} and C^{14} activity. The ratio of middle- to terminal-labeled allene or methylacetylene (no attempt was made to distinguish between 1-C^{11} and 3-C^{11}) was calculated in two ways for each run: (1) from the iodoform and acetone data, and (2) from the iodoform and acetic acid data. This procedure for degrading allene and methylacetylene was chosen because the chemistry and counting could be done in a few half-lives of C^{11} (20.4 min. half-life).

Materials.—The ethylene used was Phillips research grade (99.2% minimum purity). Neon used in the moderator experiments was Matheson research grade. Both gases were used without further purification. Allene used as a carrier gas was purchased from the Columbia Organic Chemicals Co. and from the Matheson Co. It was purified by gas chromatography before use. The methylacetylene used as carrier was purchased from the Matheson Co. (98% minimum purity) and was used without purification. 1,3-C^{14}-Acetone was obtained from New England Nuclear and Nuclear-Chicago. This material was checked for purity by vapor chromatography, counting the effluent in the standard way.[11]

Irradiation.—Irradiations were performed with the 40-Mev. Bremsstrahlung beam of the Yale University electron accelerator to form C^{11} by the $C^{12}(\gamma,n)C^{11}$ process. The samples were irradiated in Pyrex vessels. Liquid samples and the low-temperature, neon-moderated sample were cooled in pentane mush ($-130°$), and the solid samples were cooled in liquid nitrogen ($-196°$).

Separation and Degradation.—For the allene degradation, carrier allene was added to the irradiated sample, and the allene was separated from the other products of C^{11} reactions by gas chromatography on a 13-ft. 30% dimethylformamide column at 0°. After separation, the allene was allowed to flow slowly over a reaction mixture of H_2SO_4, H_2O, and Ag_2SO_4 on silica gel[13,14] at about 192° to form acetone by hydrolysis. The yield in this step was roughly 50%. The acetone was collected in an acidic iodine–iodide solution (at 0°). This solution was purged with unlabeled allene to remove any C^{11}-allene that had not reacted to form acetone.

1,3-C^{14}-Acetone was added to the solution containing the C^{11}-acetone produced by the hydrolysis. After mixing, an aliquot of this solution was taken and analyzed for C^{11} and C^{14}. The C^{14} tracer was used in this and subsequent steps to determine yields.

Sodium hydroxide solution and hydrochloric acid were added alternately to the remaining solution to precipitate iodoform five times. The sample was centrifuged after each precipitation. The precipitated iodoform was washed with a saturated aqueous solution of sodium acetate, centrifuged, and dissolved in either chloroform or, in later experiments, in ethylbenzene.[15] The iodoform fractions were kept in the dark to prevent photochemical decomposition. The iodoform fraction was counted for C^{11} and C^{14}.

The supernatant liquid from the iodoform test was extracted several times with a saturated solution of iodoform in chloroform. In this way, radioactive iodoform was removed from the supernate. After the extraction, a large excess of acetone was added to the aqueous layer, and acetone was distilled from a basic

(11) C. MacKay and R. Wolfgang, Radiochim. Acta, 1, 42 (1962).

(12) J. Dubrin, C. MacKay, and R. Wolfgang, J. Am. Chem. Soc., 86, 4747 (1964).

(13) H. M. Stanley, J. E. Youell, and J. B. Dymack, J. Soc. Chem. Ind., 53, 205T (1934).

(14) The reaction mixture consisted of 20 ml. of the inhomogeneous mixture of 5 g. of Ag_2SO_4, 29 ml. of H_2O, and 38 ml. of H_2SO_4 on 50 g. of silica gel (28–200 mesh).

(15) The C^{14} activity in the solution of iodoform in chloroform decreased with time, presumably due to decomposition of the iodoform. Thus, a correction for the decrease was required. The decomposition in ethylbenzene was negligible in the time of the experiment.

TABLE II

YIELDS OF AND C^{11} DISTRIBUTION IN ALLENE AND METHYLACETYLENE FROM CARBON REACTION WITH C_2H_4 UNDER VARIOUS CONDITIONS

| | | | Allene | | Methylacetylene | |
Sample composition	Pressure, atm. at 25°	Temp., °C.	Yield[a]	Center labeled/ terminal labeled	Yield[a]	Center labeled/ terminal labeled
C_2H_4 (gas)	2	25	16.5 ± 2.0	1.8 ± 0.1	4.5 ± 0.5	0.5 ± 0.1
C_2H_4 (liquid)		−130	11.5 ± 1.5	2.0 ± 0.2	4.0 ± 1.0	0.6 ± 0.1
C_2H_4 (solid)		−196	11.2 ± 1.2	2.1 ± 0.2	4.0 ± 1.0	0.6 ± 0.1
95% Ne, 5% C_2H_4	1	25	10.5 ± 2.0	3.2 ± 0.3	5.0 ± 0.5	
95% Ne, 5% C_2H_4	2	−130		3.4 ± 0.3		
90% Ne, 10% C_2H_4	2	25	11.0 ± 2.0		5.3 ± 0.5	1.9 ± 0.4

[a] % total volatile activity.

TABLE III

SUMMARY OF YIELDS[a] OF ALLENE, ACETYLENE, AND C_5 COMPOUNDS UNDER VARIOUS CONDITIONS

Product	C_2H_4, 76 cm.	C_2H_4, 73 cm. O_2, 3 cm.	C_2H_4, 4 cm. Neon, 76 cm.	C_2H_4, liquid	C_2H_4, solid
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	4.3 ± 0.5
Acetylene	38.5 ± 3.0	35.0 ± 1.5	17.5 ± 2.0	17.5 ± 2.0	19.5 ± 2.0
C_5 compounds	11.0 ± 2.0	<1.5	41.5 ± 2.0	25.6 ± 2.0	32 ± 4

[a] % total volatile activity.

TABLE IV

YIELDS OF CENTER AND TERMINAL C^{11}-ALLENE AND -METHYLACETYLENE

| | | | | | Yields[a] | | 2-C^{11}-Allene/ | 1-C^{11}-Allene/ |
| | | Pressure, | Allene | | Methylacetylene | | 2-C^{11}-methyl- | 1,3-C^{11}-methyl- |
Sample composition	Temp., °C	atm. at 25°	Center	Terminal	Center	Terminal	acetylene	acetylene
C_2H_4 (gas)	25	2	10.6	5.9	1.5	3.0	7.1	2.0
C_2H_4 (liquid)	−130		7.7	3.8	1.5	2.5	5.1	1.5
C_2H_4 (solid)	−196		7.6	3.6	1.5	2.5	5.1	1.4
95% Ne, 5% C_2H_4	25	1	8.0	2.5			2.8	1.6
90% Ne, 10% C_2H_4	25	2			2.9	1.6		

[a] % total volatile activity.

solution. This removed radioactive acetone from the solution. The solution was acidified, carrier acetic acid was added, and the acetic acid was distilled and collected. More acetic acid was added to the solution and the distillation was repeated. An aliquot of the distilled acetic acid fraction was counted for C^{11} and C^{14}.

The procedure for the methylacetylene degradation was similar to that for the allene degradation. After irradiation, carrier was added to the sample and the C^{11}-methylacetylene was separated by gas chromatography. A 2.5-ft. 30% dimethylformamide column at 0° or a 10-ft. nonactivated alumina column was used. The methylacetylene was hydrolyzed to acetone by slowly flowing it over a reaction mixture of $HgSO_4$, H_2SO_4, and H_2O on silica gel[16] at ~60°. The yield was about 25%. The acetone formed in the hydrolysis was trapped in the iodoform test solution at 0°. The solution was purged with methylacetylene to remove any C^{11}-methylacetylene in the solution. The rest of the procedure was the same as in the allene degradation.

Counting.—Samples were assayed for C^{11} using a standard γ-well counter with either a multi- or single-channel analyzer centered on the 0.51-Mev. positron-annihilation peak. Each sample was followed over several half-lives. Backgrounds were subtracted, and the activities were plotted and extrapolated back to a common time. This provided a measure of the relative C^{11} activities of the samples.

After decay of the C^{11} the relative C^{14} content of the samples was determined by counting a small aliquot (100 λ) in duplicate in a liquid scintillation counter. The counting efficiency of each sample was determined by adding an internal standard. From the background, sample count rate, and efficiency determination, the relative amount of C^{14} in each of the samples was determined. This information was used to correct the C^{11} measurements of the same samples for chemical yields of the degradation procedure.

Calculations.—The ratio of middle-C^{11} to terminal-C^{11} activity was calculated in two ways for each run: (1) from the iodoform and acetone data, and (2) from the iodoform and acetic acid data.

(16) The reaction mixture was 25 ml. of the inhomogeneous mixture of 0.5 g. of $HgSO_4$, 5.5 ml. of H_2SO_4, and 100 ml. of H_2O on 50 g. of silica gel (28–200 mesh).

Errors.—The major errors involved in the experiments were in the counting. The approximate errors for each of the three fractions were ±5% for C^{11} activity and ±3% for C^{14} activity. The other errors involved in the experiments (aliquoting, and contamination of the fractions by another radioactive compound) were small compared to the counting errors. The agreement between the two methods of calculation for each run, and between separate runs, was good and was within the estimated experimental errors given in Table II.

Results

A summary of the yields of allene and other relevant products under various conditions is presented in Tables II and III. The data of Table III are discussed more fully in the accompanying paper.[12]

The results of the allene and methylacetylene degradations are presented in Tables II and IV. As discussed under calculations, these results were obtained from data on the activity of acetone, iodoform, and acetic acid fractions. This permits two partially independent methods of calculation and provides an internal-consistency check. In all cases the agreement between the two methods of calculation is well within the estimated limits of experimental error based on counting statistics. With the exception of the degradation of allene formed from gaseous ethylene, the results given in Table II are the averages of the two methods of calculation for one degradative run. The result for the allene degradation in the gaseous ethylene system is the weighted average of five separate runs, in contrast to the other results, and the error is statistical (95% confidence level).

Table II shows that most of the allene produced is center labeled and that this distribution is essentially independent of phase effects. With the addition of neon moderator the 2-C^{11}-allene increases appreciably

from 64% in pure gaseous ethylene, to 76%. This distribution is unaffected by cooling the neon–ethylene sample from 25 to −130°. The percentages of center and terminal C^{11}-allene relative to the total volatile activity[17] are indicated in Table IV. Both decrease in going from the gas phase to the condensed phase and upon the addition of neon moderator.

In pure ethylene the major contribution to methylacetylene activity is from end-labeled C^{11}-methylacetylene. The pattern of change in C^{11} distribution in methylacetylene is similar to that in allene. No important phase effect is observed. However, in the 90% neon–10% ethylene sample the ratio of the yield of center- to end-labeled C^{11}-methylacetylene is 2 : 1 in contrast to the 1 : 2 ratio observed in pure ethylene. Thus, as the ratio of neon to ethylene changes, center labeling becomes more important in methylacetylene and the distribution of C^{11} in methylacetylene becomes more like that in allene.

The ratios 2-C^{11}-allene/2-C^{11}-methylacetylene and 1-C^{11}-allene/1,3-C^{11}-methylacetylene are also given in Table IV. Both ratios are greater than one under all experimental conditions. While the ratio 1-C^{11}-allene/1,3-C^{11}-methylacetylene is constant within experimental error, the ratio 2-C^{11}-allene/2-C^{11}-methylacetylene shows a threefold change on going from pure ethylene to samples with high neon/ethylene ratios.[18]

Discussion

In attempting to account for these results a large number of possible reaction paths of carbon and ethylene were considered. Most of these proved to be inconsistent with some of the data and were discarded. In this discussion we will restrict ourselves to the two complementary mechanisms which we have found to be fully in accord with all our results and with other related studies. Despite the basic simplicity of these mechanisms, the detail that must be considered makes the structure of some of the supporting arguments fairly complex. For this reason the discussion is divided as follows: (A) the structure of the primary adducts and their modes of decomposition and stabilization; (B) the electronic configuration of the reacting carbon and the primary adducts; (C) a consideration of the energy— both potential and translational—brought into the reaction and the manner of its dissipation; (D) a summary.

(A) **Proposed Mechanisms.**[19]—Two mechanisms have previously been postulated for the formation of allene from ethylene.[2,5] The first (mechanism I) involves attack at the carbon–carbon double bond to give the cyclopropylidene intermediate I.[20] Unless such in-
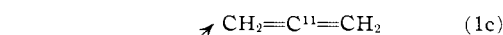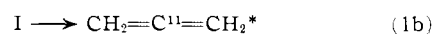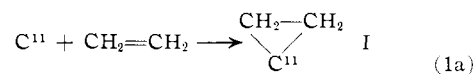
termediates are suitably substituted, their preferred mode of reaction seems to be swift collapse to allene.[21] Indeed, Shechter has reported evidence on the collapse of cyclopropylidene itself.[22]

$$C^{11} + CH_2=CH_2 \longrightarrow \begin{array}{c} CH_2-CH_2 \\ \diagdown \diagup \\ C^{11} \end{array} \quad I \qquad (1a)$$

$$I \longrightarrow CH_2=C^{11}=CH_2{}^* \qquad (1b)$$

$$CH_2=C^{11}=CH_2{}^* \diagup \begin{array}{c} CH_2=C^{11}=CH_2 \qquad (1c) \\ \\ CH\equiv C^{11}-CH_3{}^{23} \qquad (1d) \end{array}$$

The second mechanism was postulated as a consequence of experiments with alkanes.[3] It is insertion of a carbon atom into a carbon–hydrogen bond, to give an intermediate II which can then rearrange to allene or methylacetylene. (Alternatively adduct II may de-

$$C^{11} + CH_2=CH_2 \longrightarrow \begin{array}{c} H_2C=CH-\ddot{C}^{11}H \qquad (2a) \\ \updownarrow \qquad\qquad II \\ H_2\dot{C}-CH=\dot{C}^{11}H \end{array}$$

$$II \diagup \begin{array}{c} CH_3-C\equiv C^{11}H \qquad (2b) \\ \\ CH_2=C=C^{11}H_2 \qquad (2c) \end{array}$$

compose or react further.)

Both of these mechanisms are consistent with the finding that C^{11}-allene formed from mixtures of C_2H_4 and C_2D_4 consists of 87% or more $C_2C^{11}H_4$ and $C_2C^{11}D_4$,[6] i.e., that allene is formed by interaction with a single ethylene molecule.[19] Most other possible mechanisms for allene formation do not meet this condition.

The π-Bond Insertion Mechanism.—Table II shows that most of the allene formed is center labeled. No mechanism other than π-bond attack has yet been advanced which provides a satisfactory explanation of this finding. The possibility that a center-labeled adduct is produced by rearrangement of an initial complex formed by C–H bond insertion seems very unlikely. This is indicated by the finding that carbon atom attack on ethane leads to propylene which is almost completely end labeled.[24] Further support for the absence of such rearrangement is provided by the present data.[25]

(17) % ([center C^{11}-allene]/[total C^{11}-allene]) × % yield = % yield center C^{11}-allene relative to total volatile activity.

(18) In this comparison we use data for allene from a 95% neon run and for methylacetylene from a 90% neon run. Thus the reported ratio 2-C^{11}-allene/2-C^{11}-methylacetylene is significant only in establishing a qualitative trend. Since the data indicate that the yield of 2-C^{11}-methylacetylene increases as the ratio of neon to ethylene increases, at 95% neon the yield of 2-C^{11}-methylacetylene would be even higher than at 90%, and the ratio 2-C^{11}-allene/2-C^{11}-methylacetylene would be less than 2.8. Therefore 2.8 represents an upper limit for this ratio in a well moderated system.
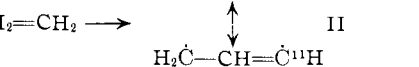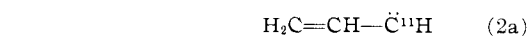
(19) See ref. 12, Appendix.

(20) Similar mechanisms have been proposed for the reaction of CH_2 with alkenes [W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, J. Am. Chem. Soc., **78**, 3224 (1956)]; for the reaction of O atoms with alkenes [R. J. Cvetanovic, Can. J. Chem., **36**, 623 (1956), and J. Chem. Phys., **30**, 19 (1959)]; in the reaction of C_2O with ethylene [K. Bayes, J. Am. Chem. Soc., **84**, 4077 (1962), and R. T. Mullen and A. P. Wolf, ibid., **84**, 3214 (1962)]; and in the reactions of S atoms with ethylene [O. P. Strausz and H. E. Gunning, ibid., **84**, 4080 (1962).]
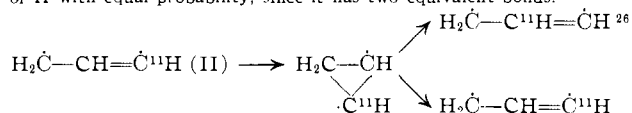
(21) For recent discussions see W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., ibid., **85**, 2754 (1963), and W. R. Moore and H. R. Ward, J. Org. Chem., **27**, 4179 (1962). Presumably these workers were dealing with singlet cyclopropylidenes. As we shall see there is some reason to believe that the cyclopropylidene intermediate formed in the reaction of carbon atoms with ethylene is also a singlet. The collapse of unsubstituted cyclopropylidenes to allenes is usually much faster than their addition to olefins. This explains our failure to find spiropentane as a product in this system. (See ref. 12.)

(22) Quoted as a private communication from S. S. Rawalay in L. Friedman and H. Shechter, J. Am. Chem. Soc., **83**, 3159 (1961). See also H. Shechter, Abstracts, 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 15-O.

(23) This isomerization of allene to methylacetylene was not specifically discussed in the earlier work.

(24) M. Marshall, unpublished.

(25) The most plausible route for rearrangement of an initially end-labeled adduct such as II would be through cyclization. The intermediate resulting from such a cyclization should then rupture to center- and end-labeled forms of II with equal probability, since it has two equivalent bonds.

$$H_2\dot{C}-CH=\dot{C}^{11}H \text{ (II)} \longrightarrow H_2C-\dot{C}H \begin{array}{c} \diagup H_2\dot{C}-C^{11}H=\dot{C}H \,{}^{26} \\ \diagdown \diagup \\ \dot{C}^{11}H \diagdown H_2\dot{C}-CH=\dot{C}^{11}H \end{array}$$

If this were the only mode of formation of center-labeled allene the ratio of center- to end-labeled allene would be less than one. Since the experimental ratio is always much greater than one (Table II), a specific involvement of the π-bond is indicated.

(26) We do not consider rupture of the third bond in this cyclic intermediate because this is a much higher energy process.

The center-labeled adduct I, formed by π-bond insertion (reactions 1a,b) can be collisionally de-excited to 2-C^{11}-allene (reaction 1c) or can rearrange to 2-C^{11}-methylacetylene (reaction 1d). Substitution of neon for ethylene reduces the efficiency of collisional-energy transfer from these adducts, thereby favoring isomerization to methylacetylene, and should therefore, decrease the ratio $CH_2C^{11}CH_2/CH_3C^{11}CH$.[27] Table IV shows that this is the case. The ratio is threefold lower in ethylene containing 90–95% neon than in pure ethylene at the same pressure.[18]

The C–H Bond Insertion Mechanism.—The data on end labeling in Table II indicate that the C–H bond insertion mechanism always contributes part of the allene yield and, except for the neon moderated samples, most of the methylacetylene yield. The alternate possibility that end-labeled allene and methylacetylene result principally from a rearrangement of an initial π-bonded adduct can be excluded.[28]
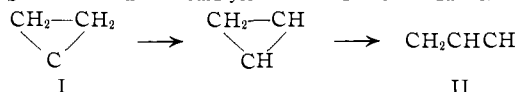
The end-labeled adduct II, formed by C–H bond insertion (reaction 2a), can rearrange to methylacetylene and allene (reactions 2b,c). Since the energy requirements for these two similar processes cannot be much different, to a first approximation the competition between those two modes of rearrangement must be independent of collisonal deactivation and their ratio should remain constant under all conditions, including dilution by neon. This ratio (see Table IV) ranges from 1.4 to 2.0, which is essentially constant within experimental error. This is in striking contrast to the threefold variation involving center-labeled products (as discussed in the section on the π-bond mechanism).[29]

Further important evidence for the C–H bond insertion mechanism (reaction 2) is provided by the identification of vinylcyclopropane in the small but significant yield of 1.5%.[12] This is just the product to be expected from reaction of the carbene adduct II with ethylene.[21,22,30] Indeed Frey has observed the analogous reaction with ethylidene.[30] He has also found that hydrogen atom shifts in carbenes related to II occur at a faster rate than does addition to olefins.[30,31] The same relationship is found in this system—the yields of end-labeled allene and methylacetylene are substantially higher than that of vinylcyclopropane.

(B) Electronic State of Allene Precursors.—From the preceding discussion it would appear that the postulated π-bond and C–H bond insertion intermediates (eq. 1 and 2) are uniquely in accord with all facets of the data and with related results from other systems. Although the evidence for the electronic state of these

precursors is not as compelling as that for their structure, it is sufficiently substantial to be worth discussing.

As mentioned above, the resonance rule indicates that both singlet and triplet (ground-state) carbon atoms are probably present as reactants.[32] The $C(^3P)$ and $C(^1D)$ atoms would be expected to behave differently in adding to ethylene. We shall postulate that the precursors of a major fraction of the acetylene and of the C_5 compounds are triplets.

$$C(^3P) + C_2H_4 \longrightarrow C_3H_4(T) \begin{array}{c} \nearrow C_2H_2 \\ \searrow \\ C_5 \text{ compounds} \end{array} \qquad (3)$$
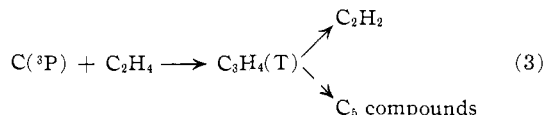
Contrasting properties of allene suggest that it is formed mainly from a singlet carbon atom.

$$C(^1D) + C_2H_4 \longrightarrow C_3H_4(S) \qquad (4)$$
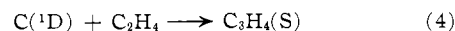
Such a scheme has appeal on the basis of the spin-conservation principle. Bond rupture to give acetylene and other degraded products[12] can dispose of the spin of the triplet adduct (eq. 3). Alternatively, the radical character of this adduct can lead to reaction with ethylene to produce C_5 compounds and higher polymers.[12] On the other hand, there is no spin restriction on the immediate rearrangement of the singlet adduct to give C_3 compounds as final products (eq. 4). As stated above, cyclopropylidene, the radical resulting from addition to the π-bond of ethylene, collapses quickly to center-labeled allene.[21,22]

The following aspects of the data are consistent with and support this hypothesis. (1) The major products seem to divide naturally into two main classes: (a) acetylene and the C_5 compounds; and (b) allene. Upon going from gaseous to condensed ethylene the yield of acetylene decreases[12] while that of the C_5's increases (Table III). This is consistent with enhanced collisional deactivation and consequent decrease in decomposition of a common precursor as in eq. 3. A similar inverse relationship is found upon neon moderation (Table III) and also suggests a common precursor for acetylene and the C_5's. (The probable reasons for this effect of neon are discussed below.) On the other hand, the allene yield is much less sensitive to phase changes and also behaves differently on moderation,[12,37] suggesting that it may have a different precursor.

(2) The addition of oxygen scavenger eliminates production of C_5 compounds, but does not affect the allene yield significantly (Table III). This suggests

(27) This effect on the fate of the excited adduct formed by reaction of a carbon atom with ethylene must be clearly distinguished from the effect of neon in reducing the average translational energy of the carbon atom *before* it reacts with C_2H_4. We shall reserve the term *moderator effect* for this second process. The moderator effect is further discussed in section C of the Discussion.

(28) Such a mechanism would yield adduct II from adduct I.

CH₂—CH₂　　　CH₂—CH
　　\ /　　　　　\ /　　　→　CH₂CHCH
　　 C　　　　　　CH
　　 I　　　　　　　　　　　II

This is unlikely in view of the properties of I. Further it would predict equal yields of center- and end-labeled methylacetylene. Since mechanism 1 can also yield $CH_3C^{11}CH$, the ratio $CH_3C^{11}CH/CH_3CC^{11}H$ would *always* have to be greater than one. Table II shows this is not so.

(29) The higher yield of end-labeled allene relative to end-labeled methylacetylene indicates a preference for migration of the hydrogen atom toward the carbon with higher electron density in adduct II.

(30) H. M. Frey, *J. Chem. Soc.*, 2293 (1962).

(31) H. M. Frey, *ibid.*, 3514 (1963).

(32) The most convincing evidence that singlet carbon atoms play a role in hydrocarbon systems comes from an examination of the data on hydrogen abstraction by carbon atoms. Such a process should lead successively to C H and C H₂ as reactive entities. The evidence that C H₂ plays an important role in these systems is substantial.[33,34] The abstraction of hydrogen from ethane and ethylene by a ground state $C(^3P)$ atom is endothermic.[34] Therefore, in analogy to observations in other systems,[35,36] neon moderation would be expected to cause a decrease in the yield of CH and of CH₂ if a $C(^3P)$ atom is the precursor of these species. In fact, the yield of propane from ethane[37] has been found to be almost independent of the neon/ethylene ratio. The simplest explanation of this result is that an electronically excited singlet carbon atom is involved.

(33) G. Stöcklin and A. P. Wolf, *J. Am. Chem. Soc.*, **85**, 229 (1963). This article contains references to earlier work. G. Stöcklin, H. Stangl, D. R. Christman, J. B. Cumming, and A. P. Wolf, *J. Phys. Chem.*, **67**, 1735 (1963).

(34) B. E. Knox and H. B. Palmer, *Chem. Rev.*, **61**, 247 (1961).

(35) P. Estrup and R. Wolfgang, *J. Am. Chem. Soc.*, **82**, 2661, 2665 (1960).

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

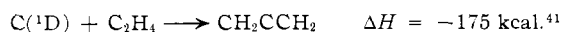(37) H. E. Rosenberg, this laboratory, unpublished results.

that the C_5 compounds and allene have different precursors, and that the C_5 precursor is a radical which reacts much more efficiently with oxygen than with ethylene.[38]

(3) As has been discussed previously, the bulk of the allene produced from mixtures of C_2H_4 and C_2D_4 is isotopically pure.[6] This finding that the primary adduct can form a product without bond rupture is consistent with spin conservation in a singlet system. These results show that a C_3 adduct does not have to undergo bond rupture simply by virtue of its excess internal energy as derived from carbon atom addition (at least under the conditions of these experiments). This in turn implies, particularly for moderated systems, that decomposition of C_3 adducts to acetylene and other products may largely be due to their electronic excitation or spin rather than their total energy content. The fact that formation of acetylene and other degraded products involves bond rupture, while formation of allene does not, can thus be associated with the hypothesis that the former derive largely from $C(^3P)$ and the latter from $C(^1D)$ atoms.[39]

Since most of the allene is center labeled and since we believe that allene precursors are largely singlet, it is tempting to associate singlet carbon atoms with π-bond insertion and triplet carbon atoms with C–H bond insertion. However, this would almost certainly be a misleading oversimplification. There is no reason to exclude some singlet C–H bond insertion. This may be the principal source of end-labeled C_3's. Similarly, π-bond insertion by triplet carbon is a likely process, although, for the reasons just discussed, the adduct formed is more likely to decompose, or add to ethylene, or both, than stabilize to give allene.

In any case, it is clear that while these hypotheses as to the excitation states of the carbon atoms are plausible and find support in the data, they should be considered as tentative and subject to probable modification and elaboration.

(C) **Energy Considerations. Effect of Neon Moderator.**—We now turn to the question of whether these reactions are driven primarily by the intrinsic reactivity of the carbon atom, or by the excess translational energy that it derives from its hot-atom origin. The high chemical potential of atomic carbon makes allene formation a highly exoergic process, even for thermal carbon atoms[40]:

$$C(^3P) + C_2H_4 \longrightarrow CH_2CCH_2 \qquad \Delta H = -138 \text{ kcal.}[41]$$

$$C(^1D) + C_2H_4 \longrightarrow CH_2CCH_2 \qquad \Delta H = -175 \text{ kcal.}[41]$$

As we have already observed, collisional deactivation

(38) Despite the fact that the C_5 yield is affected by O_2 while the acetylene yield is not these compounds can have the same original carbon atom–ethylene adduct as a precursor. If this precursor is to decompose directly to acetylene, it must do so before collisional deactivation and therefore before it can be scavenged. The alternate route, leading to C_5, will necessarily involve long-lived and therefore scavengeable radicals.

(39) Acetylene and C_6 products are more abundant than allene. It would therefore seem that more C atoms reach the chemical energy range as $C(^3P)$ than $C(^1D)$. Such a conclusion cannot be firmly predicted on the basis of resonance rule considerations (Table I) but is consistent with them.

(40) In this work, a thermal carbon atom does not mean a carbon atom in thermal equilibrium with its surroundings, but only a carbon atom with an energy in the thermal range. The reactivity of carbon atoms appears to be so high that it is unlikely that a carbon atom would undergo enough collisions to reach thermal equilibrium before reacting.

(41) Values were taken from "Selected Values of Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44.

appears to be sufficiently fast at ordinary pressures to permit de-excitation of a large fraction of these adducts without extensive bond rupture or hydrogen atom migration.

The usual method of investigating the effect of excess translational energy on atomic reactions is by the use of moderators, usually noble gases.[35] Moderators remove excess translational energy from the atom in nonreactive collisions, and thereby reduce the average energy at which these atoms can react. The validity of this approach has been demonstrated in experiments with hot hydrogen atoms, and, indeed, has proven susceptible to a quantitative treatment by the use of a recently derived kinetic theory of hot-atom reactions.[35,42] Moderator effects on carbon atom reactions have also been observed.[12,36,37] Tables II and III show results of experiments in which the amount of neon was sufficiently large to make it likely that most reactions occurred at thermal energies.

The addition of neon will have other effects besides moderating the carbon atom: (a) Poorer collisional deactivation of excited intermediates; evidence for this is provided by the decrease in yields of C_3 products, and the increase in isomerization of 2-C^{11}-allene to 2-C^{11}-methylacetylene as previously noted. (b) A modification in the ratio of $C(^1D)$ to $C(^3P)$ atoms; this is to be expected as a result of the change in the nature and number of collisions that a carbon atom makes before it reacts. An increase in the number of $C(^3P)$ (ground state) atoms could, in part, account for the decrease in the sum yield (allene + methylacetylene) in neon-moderated systems (Table III).[43]

Despite these other factors the neon results do permit some definite conclusions as to the involvement of translational energy in the reactions: (1) Even in highly moderated systems the same products are found as in unmoderated systems, but in different yields. This implies that a thermal atom can react by almost all of the modes available to a hot atom. The reactivity of a carbon atom thus appears to be intrinsic. In view of its high chemical potential this finding that the excess translational energy is of secondary importance is not surprising. (2) The ratio of center- to end-labeled C_3 products is greater in moderated than in unmoderated systems. This implies that thermal carbon atoms are more selective in attacking the π- rather than the C–H bond.[44] (3) The ratio of C_5 compounds to acetylene increases in the presence of neon. If the only effect of the neon were to reduce the efficiency with which the common precursor of these products is deactivated (eq. 3), this ratio would be expected to remain the same or perhaps to decrease.[12] Therefore, it appears that the role of neon as a moderator for carbon atoms is dominant. If a carbon atom is thermalized, the adduct it forms is less excited, less likely to decompose to acetylene, and more likely to undergo a reaction sequence involving ethylene which leads to C_5 compounds.[12]

The qualitative similarity of products in moderated and unmoderated systems tells us that thermal and hot carbon atoms can react similarly. The quantitative

(42) R. Wolfgang, J. Chem. Phys., **39**, 2983 (1963).

(43) Analogous effects have been noted for methylene: F. A. L. Anet, R. F. W. Bader, and A. M. Van der Auwera, J. Am. Chem. Soc., **82**, 3217 (1960); H. M. Frey, ibid., **82**, 5947 (1960).

(44) A similar result for the effect of energy on the selectivity of CH_2 reactions has been observed: J. N. Butler and G. B. Kistiakowsky, ibid., **82**, 759 (1960).

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 π-bond of ethylene. This reaction can occur by the addition of a carbon atom to the π-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 π-bond and C–H bond insertion reactions of carbon atoms have very low activation energies.

Reactions of Carbon Atoms with Ethylene. II. Production of Acetylene and C₅ Compounds

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

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 C₅ 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 C₅, 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 ($\sim$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 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).