# Bond Energy Effects and Acetylene Production in the Reactions of Energetic Carbon Atoms with Alkyl Halides and Propane[1]

**Hans J. Ache and Alfred P. Wolf**[2]

*Contribution from the Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973. Received September 3, 1965*

**Abstract:** One of the products formed in the reactions between energetic carbon atoms and hydrocarbons or alkyl halides is acetylene. Eighty-five per cent or more of the acetylene-$C^{11}$ produced from the specifically deuterated hydrocarbons $CD_3CH_2CH_3$, $CH_3CD_2CH_3$, and $CD_3CH_2CD_3$ or from the deuterated alkyl halides $CD_3CH_2X$ and $CH_3CD_2X$ by reaction with hot carbon-11 atoms ($N^{14}(p,\alpha)C^{11}$) is either isotopically pure $HC^{11}{\equiv}CH$ or $DC^{11}{\equiv}CD$. The deuterium label serves as a probe for the point of attack of the hot carbon atom. A regular increase in the proportion of the hot yield as acetylene from the $-CH_2X$ group, where X is $CF_3$, F, Cl, Br, and I, is noted. The increasing yield pattern is proportional to the decreasing bond dissociation energy, where the largest percentage of the hot products as acetylene is shown to come from the $-CH_2I$ group. This further supports the "excitation-decomposition" mechanism in which the influence of "bond dissociation" energy on product formation is demonstrated for acetylene. In addition the ratio of acetylene production $[HC^{11}{\equiv}CH]_{CH_3}/[HC^{11}{\equiv}CH]_{CH_2}$ is $\cong 1.9$/group for the compounds investigated.

The reactions of energetic carbon atoms produced by nuclear reactions has been studied in numerous systems. Results and postulated reaction mechanisms are the subject of recent reviews.[3,4]

The mechanistic approach to the reactions of energetic (or "hot") carbon atoms is currently formulated in terms of insertion reactions by carbon atoms, methyne, and methylene (*cf.* ref 3 and 4). The "primary" process leading to ultimate product formation must, of course, be the collision of a carbon atom with the substrate molecule. The results of this collision can be an isolable product produced in a stepwise fashion, or the collision can result in a reactive intermediate which still contains excess energy albeit not necessarily in kinetic form alone. The reactive intermediates, methyne and methylene (and possibly methyl radicals), products of fragmentation and abstraction reactions, can be considered as primary reagents even though the "true" primary event involves collision between the carbon atom and the substrate only. Some carbon atoms and indeed some of the other highly reactive fragments formed can lose all of their excess kinetic energy and be in their normal ground states before reaction resulting in isolable species takes place. These thermal reactions are not considered in this paper. The insertion hypothesis serves to rationalize a good deal of what is observed in simple organic systems. Stable products accounting for a major fraction of the energetic carbon-11 atoms produced in some organic systems are labeled acetylene, ethylene, and certain homologs of the substrate. Some of the minor products, particularly reentry products,[5] have not been adequately accounted for by the insertion hypothesis or any other postulated mechanism.

It was suggested by MacKay, *et al.*,[6] that the insertion by an energetic carbon atom into a carbon-hydrogen bond was the first step leading to the formation of acetylene in hydrocarbon systems. Phase effect studies[7] (*cf.* also ref 3 and 8) showed that the initial complex formed by the reaction of an energetic carbon atom with an alkane had a lifetime long by comparison with a bond vibration and could be collisionally deactivated. This suggested that the energy of some of the complexes might be low enough so that bond-energy effects might affect the "excitation-decomposition" sequence.

In order to investigate the effect of bond energy on acetylene production, it was necessary to be able to relate a particular yield of acetylene as having arisen from a particular bond in a molecule. The separation of the various deuterated ethylenes by Cvetanović, *et al.*,[9] made possible the application of a double-tracer technique to this problem. The source of the labeled acetylene (*vide infra* for experimental technique) from reaction between a carbon atom and an alkane has been demonstrated using molecules such as $CD_3CH_3$,[10] $CH_3CD_2CH_3$, $CD_3CH_2CD_3$, and $CD_3CH_2CH_3$.[11] A minimum of 85% of the labeled acetylenes found were either $HC^{11}{\equiv}CH$ or $DC^{11}{\equiv}CD$. It was shown that the reaction was primarily intramolecular.[10,11]

It has now been possible to show that similar results obtain for specifically deuterated alkyl halides, *i.e.*, $CH_3CD_2X$ and $CD_3CH_2X$. Here again about 85% of the total carbon-11 labeled acetylene was either $HC^{11}{\equiv}CH$ or $DC^{11}{\equiv}CD$. It is most interesting to note that the over-all hot reaction was indeed sensitive to relatively small energy differences in the C–X bonds. That such an effect could be observed in "hot-atom" reactions was reported by Breckenridge, *et al.*,[12]

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[1] This research was performed under the auspices of the U. S. Atomic Energy Commission.

[2] Requests for reprints should be addressed to this author.

[3] A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 202 (1964).

[4] R. Wolfgang, *Progr. Reaction Kinetics*, **3**, 99 (1965).

[5] A. P. Wolf, *Ann. Rev. Nucl. Sci.*, **10**, 259 (1960).

[6] C. MacKay, M. Pandow, P. Polak, and R. Wolfgang in "Chemical Effects of Nuclear Transformations," IAEA, Vienna, 1961, pp 17–26.

[7] G. Stöcklin and A. P. Wolf, *J. Am. Chem. Soc.*, **85**, 229 (1963).

[8] C. E. Lang and A. F. Voigt, *J. Phys. Chem.*, **65**, 1542 (1961).

[9] R. J. Cvetanović, F. J. Duncan, and W. E. Falconer, *Can. J. Chem.*, **41**, 2095 (1963).

[10] J. Dubrin, C. MacKay, and R. Wolfgang, *J. Chem. Phys.*, **41**, 3267 (1964).

[11] H. J. Ache and A. P. Wolf, "Chemical Effects of Nuclear Transformations," Vol. I, IAEA, Vienna, 1964, pp 107–120.

[12] W. Breckenridge, J. W. Root, and F. S. Rowland, *J. Chem. Phys.*, **39**, 2374 (1964), and their prior work.

relative to the "hot" formation of HT in the reaction of energetic tritium atoms with hydrocarbons.

## Experimental Section

**Deuterated Alkanes.** The deuterated compounds, propane-1,1,1,3,3,3-$H^2{}_6$, propane-2,2-$H^2{}_2$, propane-1,1,1-$H^2{}_3$, and propane-1,1,1,2,3,3,3-$H^2{}_7$, were obtained from Merck Sharpe and Dohme, Ltd., Montreal, Canada. Deuterium analyses were provided by Merck and were also carried out at BNL. Table I gives the analytical results. The structure of the most probable impurity is based on the cracking pattern of the labeled compound. The results listed in subsequent tables have been corrected for these compositions.

Table I. Deuterium Content of Labeled Propanes

| Compound | D enrichment, % | Probable impurity (%) |
|---|---|---|
| $CD_3CH_2CD_3$ | 97.6 | $CD_2HCH_2CD_3$ (14.3) |
| $CH_3CD_2CH_3$ | 95.6 | $CH_3CDHCH_3$ (8.8) |
| $CD_3CH_2CH_3$ | 93.5 | $CD_2HCH_2CH_3$ (19.5) |
| $CD_3CHDCD_3$ | 98.0 | $CD_3CHDCHD_2$ (14.0) |

**Nitrogen and Oxygen.** Airco research grade nitrogen and oxygen were used without further purification. Mass spectrometric assay provided by the supplier indicates less than 4 ppm of impurities in each.

**Deuterated Ethyl Halides.** The specifically deuterated ethyl halides were prepared from ethanol-1,1-$H^2{}_2$ and ethanol-2,2,2-$H^2{}_3$, obtained from Merck. Deuterium analyses gave 98% enrichment for the former and 99.5% enrichment for the latter compound. The method of Edgell and Parts[13] was used in preparing the tosylate. In each case 2 g of the tosylate was dissolved in 15 cc of diethylene glycol, and 2 g of the appropriate potassium halide was added. The mixture was heated for 2 hr at 150° under a helium atmosphere. A gas-phase transfer from the reaction mixture was accomplished on a vacuum line with the compound being trapped in a liquid nitrogen cooled trap. Each halide was purified by preparative glc using a 6-ft column containing 20% oxydipropionitrile on Chromosorb W. The yields of the fluoride, chloride, bromide, and iodode were in the 60–70% range based on the purified material. Deuterium assay of the halides indicated no loss of deuterium.

**1,1,1-Trifluoropropane-2,2-$H^2{}_2$ and 1,1,1-Trifluoropropane-3,3,3-$H^2{}_3$.** Propionic acid-2,2-$H^2{}_2$ (and, correspondingly, propionic acid-3,3,3-$H^2{}_3$) obtained from Merck was treated with $SF_4$ (Matheson Co.) in a steel bomb[14] under 1 atm of helium. The product mixture was first passed through a washing tower containing 40% aqueous KOH solution, then through a drying tower containing KOH pellets, and finally through a liquid $N_2$ cooled trap. The bomb was twice more pressurized with helium at 2 atm and the isolation procedure repeated in order to assure collection of as much product as possible. The product was purified by preparative glc (*vide supra*). Final purification in this case was accomplished by means of a 10-ft column containing 30% dimethylsulfolane on Chromosorb W. A yield of about 70% was obtained for each of the two fluorides.

**Deuterated Methyl Halides.** The deuterated methyl fluoride was prepared by allowing methyl-$H^2{}_3$ iodide (Merck Sharpe and Dohme, Canada, 99 atom % deuterium in compound) to react with potassium fluoride in refluxing diethylene glycol for 4 hr. Unreacted methyl-$H^2{}_3$ iodide isolated by vacuum transfer was recycled using the same conditions until satisfactory yields were obtained (~40%). The fluoride was purified by glc using a 16-ft oxydipropionitrile column.

**Nondeuterated Compounds.** Ethyl fluoride, bromide, and iodide were research grade compounds. They were redistilled and used without further purification. The cyclopropane was Matheson CP cyclopropane.

**Irradiation Techniques.** The 10-Mev proton beam of the Brookhaven 60-in. cyclotron was used for all irradiations. The irradiations were carried out with the gas contained in a 40-cc aluminum tank with a 3-mil aluminum window. All compounds were irradiated with a 30-sec duration 5-μa beam. The gas composition in all cases was 50% organic compound, 45.5% nitrogen, and 4.5% oxygen. The total gas pressure was 760 mm except in the case of the iodide where the total pressure was 200 mm.

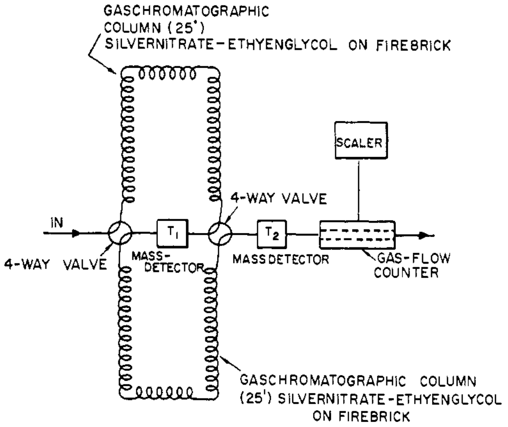

Figure 1. Recycling technique for separation of doubly labeled ethylene.

**Assay of the Isotopic Acetylene.** Carrier acetylene and acetylene-1,2-$H^2{}_2$ were added to the irradiated mixtures. The doubly labeled (*i.e.*, $C^{11}$ and $H^2$ containing) acetylenes were isolated from the bulk gas using a 40–60 mesh silica gel filled 5-mm i.d. × 2.5 m long glass column. No exchange of acetylenic hydrogen occurs on this column. The acetylenes were collected and transferred to a 25-cc glass bulb containing 5 cc of freshly prepared chromous chloride solution.[15] The method of Crompton and Woodruff[16] was used to reduce the acetylenes to the corresponding ethylenes. Shaking at room temperature for 10 min served to provide >98% reduction in every case. Four different ethylenes are produced in this reduction, only three of which are identifiable: $C^{11}H_2{=}CH_2$, $C^{11}H_2{=}CHD$ (or $CH_2{=}C^{11}HD$ which is indistinguishable from $C^{11}H_2{=}CHD$ by our method), and $C^{11}HD{=}CHD$ (no consideration is given to the possibility of *cis–trans* isomers in the last compound). A sample of pure $DC^{11}{\equiv}CD$ was reduced by this technique and only $C^{11}DH{=}CDH$ was detected as product. The sensitivity of our assay method allows us to set a maximum of 2% of other ethylenes formed by exchange if indeed any is formed. The three possible ethylenes, $C^{11}H_2{=}CH_2$, $C^{11}H_2{=}C^{(11)}HD$, and $C^{11}DH{=}CDH$, corresponding to the three acetylenes, $HC^{11}{\equiv}CH$, $HC^{11}{\equiv}C^{(11)}D$, and $DC^{11}{\equiv}CD$, were then separated using the column packing essentially as described by Cvetanović.[9] The recycling method of Root, *et al.*,[17] presented in diagrammatic form in Figure 1, was used to get the effective column length required. The columns were made of 25-ft sections of 3.5-mm i.d. 316 stainless steel. The tubing connecting the columns with the valves and the detector ($T_1$, Figure 1) was 1.5-mm i.d. 316 stainless steel with the connecting lengths being as short as possible. This was necessary in order to prevent peak spread as much as possible. The two four-way valves (Mikrotek-5-port linear valve GCL-M-4005) were also chosen for low volume. The substrate was 30–60 mesh J. M. firebrick (acid washed and then washed to neutrality) coated with 25% ethylene glycol (saturated with $AgNO_3$). The separation of a sample containing 45% $C_2H_4$, 10% $C_2H_3D$, and 45% $C_2H_2D_2$ is shown in Figure 2. When carbon-11 containing compounds were used, the carriers served to locate peak position and thus facilitated operation of the switching valves. When the desired separation had been achieved, the gas was allowed to pass through an effluent counting system and the activity in each peak was determined.[18] In the separation of the radioactive compounds, time is of the essence owing to the half-life of carbon-11 (20.4 min). For example, the recycle technique using an effective length of 100 ft (four passes) takes approximately 65% of the time required

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[13] W. F. Edgell and L. Parts, *J. Am. Chem. Soc.*, **77**, 4899 (1955).

[14] *Cf.* W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *ibid.*, **82**, 543 (1960).

[15] L. F. Audrieth, Ed., "Inorganic Syntheses," Vol III, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p 149.

[16] C. E. Crompton and N. Woodruff, *Nucleonics*, **7**, No. 3, 49 (1950).

[17] J. W. Root, E. K. C. Lee, and F. S. Rowland, *Science*, **143**, 676 (1964).

[18] G. Stöcklin, F. Cacace, and A. P. Wolf, *Z. Anal. Chem.*, **194**, 406 (1963).

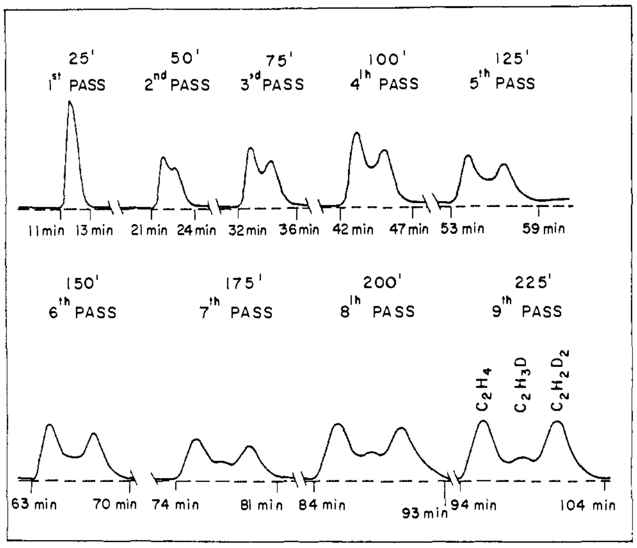


Figure 2. Separation of some deuterated ethylenes achieved by the recycle technique.

with a 100-ft column packed with the same material used in the 25-ft columns.

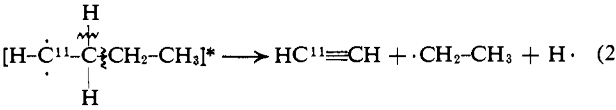
This procedure was used to determine the relative yields of the three acetylenes formed in the hot reactions.

**"Absolute" Yield of Radioactive Compounds.** Gas mixtures composed of 50% alkyl halide, 45.5% $N_2$, and 4.5% $O_2$ at a total pressure of 250 mm were irradiated with protons at 5 $\mu$a for 10 sec. The dose to the system under these conditions was about $2 \times 10^{-3}$ ev/molecule. The compounds produced were identified and assayed by the usual combined gas chromatographic–effluent counting technique.[18] The total activity produced was determined by passing known aliquots of the bulk-irradiated gas directly through the counter. Yields of $C^{11}$-labeled products from other compounds discussed in the text were determined in the usual way[18] and are given in tables and figures in the text (*vide infra*).

## Insertion Reactions

The postulated formation of acetylene *via* a first step involving carbon atom insertion[6] raises the question of the detailed stepwise procedure (if indeed it is a stepwise process) leading to the product. The reaction sequence can be formulated as eq 1 and 2. The intra-

$$[:\dot{C}\cdot^{11}]^{\ddagger} + CH_3\text{–}CH_2\text{–}CH_3 \longrightarrow [H\text{–}\underset{\cdot}{\dot{C}}{}^{11}\text{–}CH_2\text{–}CH_2\text{–}CH_3]^* \quad (1)^{19}$$



$$[H\text{–}\underset{\cdot}{\dot{C}}{}^{11}\text{–}\underset{H}{\overset{H}{C}}\text{–}CH_2\text{–}CH_3]^* \longrightarrow HC^{11}\equiv CH + \cdot CH_2\text{–}CH_3 + H\cdot \quad (2)^{20}$$

molecularity of this process has been confirmed by use of the double-label technique.[10,11] Equimolar mixtures of a series of six protonated and perdeuterated hydrocarbons gave an average yield of 6.7% of the "mixed" acetylene, $HC^{11}\equiv C^{(11)}D$.[11]

The indiscriminate action of singlet methylene in its reactions with carbon-hydrogen bonds is well known and has been discussed in numerous reviews (*cf.* ref 21 and 22). The formation of methylene by energetic carbon atom reactions and its insertion reactions has also been discussed.[3] Whether or not the carbon atom can show discrimination in its reactions with carbon–hydrogen bonds in alkanes was therefore of interest. It has been suggested by Rack, *et al.*,[23a] that carbon-11 atom insertion is largely statistical. Marshall, *et al.*,[24] have presented evidence that energetic carbon atoms prefer attack on $\pi$ bonds rather than $\sigma$ bonds.

It has been possible using the specifically deuterated molecules, $CD_3CH_2CH_3$, $CH_3CD_2CH_3$, $CD_3CH_2CD_3$, and $CD_3CHDCD_3$, to relate the origin of the observed acetylene-$C^{11}$ to the point of reaction in the molecule. The results are listed in Table II. The data show a clear preference for acetylene-$C^{11}$ production from the methyl group as opposed to the methylene group. The average value $[C_2H_2]_{CH_3}/[C_2H_2]_{CH_2}$ is $\cong$ 1.88. The ratio would be somewhat larger if corrected for isotope effect,[3,11] but, since this correction would be an approximation at best, it was not made here. The low yields of the "mixed" acetylene $[HC^{11}\equiv C^{(11)}D]$ observed in carbon-11 reactions with equimolar alkane–perdeuterated alkane mixtures,[3,11] when contrasted with the higher "mixed" acetylene yields observed from the specifically labeled propanes (*cf.* Table II), suggests that some intramolecular rearrangement is taking place in the excited "partially deuterated propane plus carbon atom" complex prior to decomposition to give acetylene. The mechanistic significance of these bond-reorganization reactions is the subject of investigations in progress. However, the predominant decomposition mode does not involve intramolecular rearrangement as a prior step, and thus the general nature of the mechanistic hypothesis for acetylene formation is not affected.

**Table II.** $C^{11}$-Acetylene Yields from Specifically Deuterated Propanes[a]

| Compound | Acetylene yields, % | | | Ratio[b] |
|---|---|---|---|---|
| | $HC^{11}\equiv CH$ | $HC^{11}\equiv C^{(11)}D$ | $DC^{11}\equiv CD$ | |
| $CD_3CH_2CH_3$ | 55.4 | 9.0 | 35.6 | 1.78 |
| $CH_3CD_2CH_3$ | 69.9 | 11.5 | 18.6 | 1.88 |
| $CD_3CH_2CD_3$ | 17.4 | 17.4 | 65.2 | 1.87 |
| $CD_3CHDCD_3$ | <2.0 | 20.2 | 79.8 | 1.98 |

[a] The results for each specifically labeled propane have been corrected for the deviations arising from the fact that each propane was not 100% isotopically pure as written in column 1. [b] $C^{11}$-Acetylene from methyl group/$C^{11}$-acetylene from methylene group.

A ratio can be derived in another way by plotting the data of Lieberman, *et al.*,[25] for some straight-chain alkanes (Figure 3). Using the value for $\Sigma CH_3 = 0$, *i.e.*, $\Sigma CH_2/\Sigma C = 1$, obtained by extrapolation of the line and using the value for $\Sigma CH_3 = 1$, *i.e.*, $\Sigma CH_3/\Sigma C = 1$, a ratio of 1.93 is obtained. The closeness of these ratios obtained in two ways is interesting in view of the

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[19] $\ddagger$ designates excess kinetic energy; * designates excess internal energy (unspecified as to type).

[20] The decomposition may be stepwise in the sense that the scission of two bonds does not necessarily occur simultaneously. It is conceivable that the fragment may last through many bond vibrations before collapsing to the final product. Detailed pressure dependence studies (*vide infra*) may shed some light on this.

[21] J. A. Bell, *Progr. Phys. Org. Chem.*, **2**, 1 (1964).

[22] P. P. Gaspar and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press Inc., New York, N. Y., 1964, pp 235–274.

[23] (a) E. P. Rack, C. E. Lang, and A. F. Voigt, *J. Chem. Phys.*, **38**, 1211 (1963). (b) D. E. Clark and A. F. Voigt, **87**, 5558 (1965), have recently obtained more data on structural dependence effects in liquid alkanes.

[24] M. Marshall, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 4741 (1964).

[25] P. Lieberman, R. Odum, and A. P. Wolf, unpublished results; *cf.* the results of (a) G. Stöcklin and A. P. Wolf, "Methods of Preparing Marked Molecules," paper presented at the Euratom meeting, Brussels, 1964; and (b) "Chemical Effects Associated with Nuclear Reactions," IAEA, Vienna, 1964, pp 121–132.

fact that neither is a true insertion ratio in the same sense as those obtained from the reactions of methylene with alkanes. The ratio based on acetylene-$C^{11}$ yields is a function of both the nature of the insertion and the nature of the decomposition mode of the excited complex. While assumptions about the statistical nature of the former can be made it is more difficult to make an assumption about the latter since we know that the excited complex can lead to other products,[3] and there is a marked influence of the structure of the substrate on this product spectrum.

The insertion step can be considered as occurring by attack directly on the CH bond, or the assumption can be made that every collision with a group, *e.g.*, methyl or methylene, results in insertion into a C–H bond of that group. The ratio, 1.9, obtained in two different ways indicates that if the initial attack by the carbon atom has any influence on product formation, the attack is on the group as a whole rather than direct attack on the carbon–hydrogen bond. This is perhaps not unreasonable when one considers that the total reaction probability for these energetic carbon atom reactions is in the range of 0.01 to 0.5. The number of collisions is relatively small (therefore each collision must have a high probability of success) in the reactive range. Once the atom is thermalized it no longer can react because it is scavenged under our reaction conditions. Multiple jeopardization of a molecule necessitated by the high-entropy factor due to the orthogonal nature of C–H bond insertion is not possible under these reaction conditions.

Another factor affecting the absolute yield of acetylene is the degree of moderation afforded by the substrate itself. There is no reason to suppose that the energy distributions of the reactive carbon atoms is the same in methane as in *n*-hexane exclusive of their mass difference. While reasonable predictions can be made about the loss of kinetic energy (and therefore the numbers of collisions a carbon atom undergoes in going from one energy to another) effected by collision with inert moderators, relatively little can be said for the numbers of collisions a carbon atom undergoes in a broad spectrum of organic substrates since the loss of energy will be due to factors in addition to those involved in simple kinetic energy transfer.

The detailed nature of this "insertion"–decomposition reaction (eq 1 and 2) is being investigated further using mixed systems, higher molecular weight specifically labeled alkanes, and inert moderator containing systems.

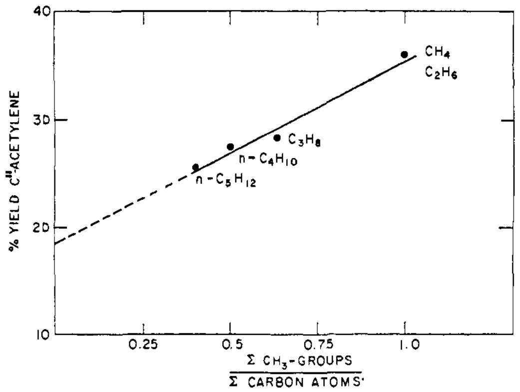
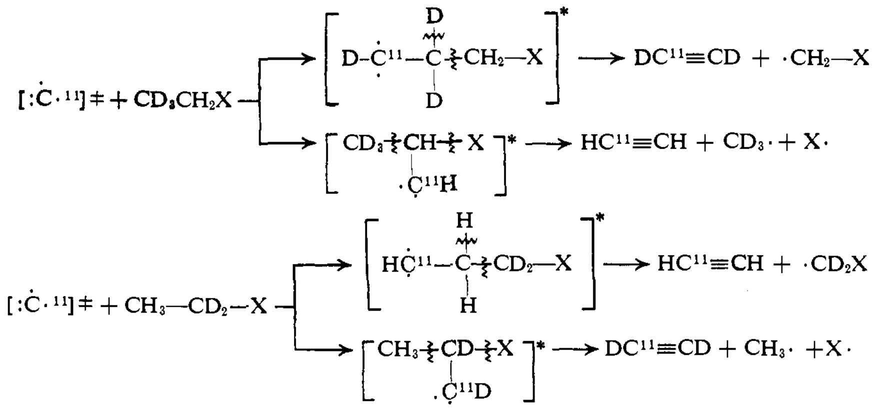


Figure 3. Acetylene yields from homologous alkanes in systems containing 94.5% alkane and 4.5% $O_2$.

**Bond Energy Effects.** The possible effect of bond energy on the decomposition step (*cf.* eq 2) in the acetylene-$C^{11}$ forming reaction was investigated in a series of experiments in which the relative yields of the isotopic acetylenes, $HC^{11}\equiv CH$, $HC^{11}\equiv C^{11}D$, and $DC^{11}\equiv CD$, were determined following the $N^{14}(p,\alpha)C^{11}$[26] reaction in ten specifically deuterated halides. Equations 3a,b and 4a,b illustrate the possibilities. The halides fluoride, chloride, bromide, and iodide were used. The two possible deuterated 1,1,1-trifluoropropanes were also included for comparison since the $RCH_2$–$CF_3$ bond strength is also known. The results are listed in Table III. The amount of mixed product is essentially constant, the average being 16%. The methyl-deuterated and methylene-deuterated compounds were run to provide an experimental method for averaging out the isotope effect in product formation.



$$[:\dot{C}\cdot^{11}]^{\ddagger} + CD_3CH_2X \rightarrow \left[ D\text{-}\dot{C}^{11}\text{—}\overset{D}{\underset{D}{C}}\text{—}CH_2\text{—}X \right]^* \rightarrow DC^{11}\equiv CD + \cdot CH_2\text{—}X \qquad (3a)$$

$$[:\dot{C}\cdot^{11}]^{\ddagger} + CD_3CH_2X \rightarrow \left[ CD_3\text{—}\underset{\cdot C^{11}H}{CH}\text{—}X \right]^* \rightarrow HC^{11}\equiv CH + CD_3\cdot + X\cdot \qquad (3b)$$

$$[:\dot{C}\cdot^{11}]^{\ddagger} + CH_3\text{—}CD_2\text{—}X \rightarrow \left[ H\dot{C}^{11}\text{—}\overset{H}{\underset{H}{C}}\text{—}CD_2\text{—}X \right]^* \rightarrow HC^{11}\equiv CH + \cdot CD_2X \qquad (4a)$$

$$[:\dot{C}\cdot^{11}]^{\ddagger} + CH_3\text{—}CD_2\text{—}X \rightarrow \left[ CH_3\text{—}\underset{\cdot C^{11}D}{CD}\text{—}X \right]^* \rightarrow DC^{11}\equiv CD + CH_3\cdot + X\cdot \qquad (4b)$$

There is a clear and unequivocal increase in the ratio $[C_2H_2]_{CH_2X}/[C_2H_2]_{CH_3}$ relative to the substituent X, as X is in the order $CF_3$, F, Cl, Br, I, ranging from 0.48 for $C_2H_5CF_3$ to 1.05 for $C_2H_5I$.

The change in ratio can be caused by a decrease in acetylene production from the methyl group, an increase in production from the methylene group, or by changes in both. A further series of runs was carried out with the five nondeuterated compounds listed in

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(26) The source of nitrogen in the system is nitrogen gas. The validity of this approach was confirmed by comparing ratios obtained in nitrogen-containing systems with those in which the $C^{12}(n,2n)C^{11}$ reaction is used, the substrate then being the source of carbon-11. In all cases the ratios obtained from the substrate + nitrogen were identical with those obtained from the substrate alone. The absolute yields of products are lower in the nitrogen-containing systems.

**Table III.** $C^{11}$-Acetylene Yields from Specifically Deuterated Alkyl Halides

| Compound | % of total $C^{11}$-acetylene[a] HC≡CH | HC≡CD | DC≡CD | $\frac{[DC^{11}\equiv CD]}{[HC^{11}\equiv CD]}$ | $\frac{[HC^{11}\equiv CH]}{[DC^{11}\equiv CD]}$ | $[C^{11}\text{-acetylene}]_{CH_2}/[C^{11}\text{-acetylene}]_{CH_3}$ | Total increase in $C^{11}$-acetylene[b] | C–X bond dissocn energy,[c] kcal |
|---|---|---|---|---|---|---|---|---|
| $CH_3CD_2CF_3$ | 57.2 | 16.9 | 25.9 | 0.45 | | 0.48 | 1.48 | 117 |
| $CD_3CH_2CF_3$ | 29.6 | 13.4 | 57.0 | | 0.52 | | | |
| $CH_3CD_2F$ | 55.5 | 18.2 | 26.3 | 0.48 | | 0.51 | 1.51 | 102 |
| $CD_3CH_2F$ | 30.0 | 15.3 | 54.7 | | 0.55 | | | |
| $CH_3CD_2Cl$ | 48.2 | 18.6 | 32.2 | 0.68 | | 0.76 | 1.76 | 78 |
| $CD_3CH_2Cl$ | 39.3 | 14.2 | 46.5 | | 0.85 | | | |
| $CH_3CD_2Br$ | 46.6 | 17.4 | 36.0 | 0.77 | | 0.88 | 1.88 | 65 |
| $CD_3CH_2Br$ | 43.0 | 13.7 | 43.3 | | 0.99 | | | |
| $CH_3CD_2I$ | 40.8 | 17.5 | 41.7 | 1.02 | | 1.06 | 2.06 | 54 |
| $CD_3CH_2I$ | 45.2 | 13.7 | 41.4 | | 1.09 | | | |

[a] The precision of the relative yields for $HC^{11}\equiv CH$ and $DC^{11}\equiv CD$ is ±0.5 unit. The precision for the mixed compound $HC^{11}\equiv C^{11}D$ is ±1.0 unit. [b] Arbitrary units. Acetylene yield = $1 + [C^{11}\text{-acetylene}]_{CH_2}/[C^{11}\text{-acetylene}]_{CH_3}$ where the yield from the methyl group is arbitrarily set = 1. [c] Values are from ref 30a and b.

**Table IV.** Absolute Acetylene Yields from $C_2H_5X$

| Compound | % of total $C^{11}$ $C^{11}O$ | $HC^{11}\equiv CH$ | $\frac{\% HC^{11}\equiv CH}{100 - \% C^{11}O}$ |
|---|---|---|---|
| $C_2H_5CF_3$ | 77.0 | 8.5 | 0.37 |
| $C_2H_5F$ | 59.1 | 15.2 | 0.37 |
| $C_2H_5Cl$ | 65.2 | 14.2 | 0.41 |
| $C_2H_5Br$ | 72.0 | 12.6 | 0.45 |
| $C_2H_5I$ | 74.5 | 11.9 | 0.47 |

Table IV, and the absolute acetylene yields[27] were measured. Scavenger oxygen was used in all of these runs in sufficient concentration (4.5 vol %) to react with all thermal carbon atoms. Thus, even though the observed yield of acetylene goes down, the yield of acetylene relative to the total hot product yield [where 100 − %$C^{11}O$ (*cf.* ref 25b) is taken as the total hot product yield] goes up. This ratio is plotted in Figure 4 against the arbitrary increase in total $C^{11}$ yield given in Table III. The excellent correlation supports the contention that the change in the ratio $[C_2H_2]_{CH_2X}/[C_2H_2]_{CH_3}$ is primarily due to an increase in acetylene yield from the methylene group and means in essence that there is no "β" effect[28] on acetylene yield in this series of compounds.

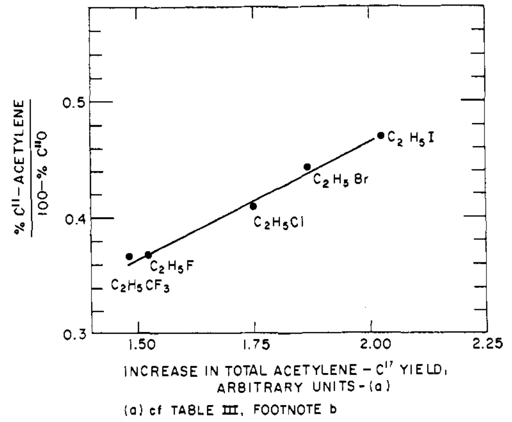

Figure 4. Increase in acetylene yield relative to total "hot" products for a series of $C_2H_5X$ compounds.

In order to investigate a possible moderator effect, methyl fluoride, methyl-$H^2_3$ fluoride, an equimolar methyl-$H^2_3$ fluoride–methyl chloride mixture, and an equimolar methyl-$H^2_3$ fluoride–methyl bromide mixture were allowed to react with carbon-11 atoms. In the cases of the mixtures, the same carbon-11 atom energy spectrum for acetylene-$C^{11}$ production obtained from moderation by a particular compound is available to both compounds, and a measure of their relative abilities to produce acetylene-$C^{11}$ is obtained. The double-label technique was used in order to determine the source of the acetylene-$C^{11}$. The results are plotted in Figure 5. Under identical conditions then, the ease of forming acetylene-$C^{11}$ from the complex relative to other hot products shows the order Br > Cl > F.

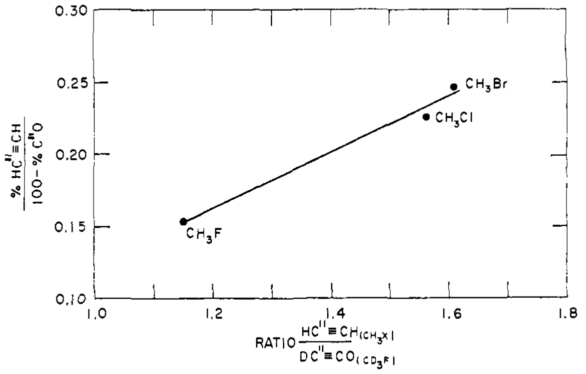

Figure 5. Relative acetylene-$C^{11}$ yields from mixed systems of methyl halides.

How insertion reactions by electrophilic species into a carbon–hydrogen bond are affected by the presence of halogen is not clearly understood. Franzen[29]

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(27) It would have been of considerable interest to measure the absolute yields in the double-label experiments, but the concentration of $C^{11}$ available from irradiation with the available BNL facilities is too low to permit simultaneous measurement of relative double-label yields and absolute yields.

(28) A β effect is here defined as the effect of X on the $CH_3$ group.

(29) V. Franzen, *Ann.*, **627**, 22 (1959).

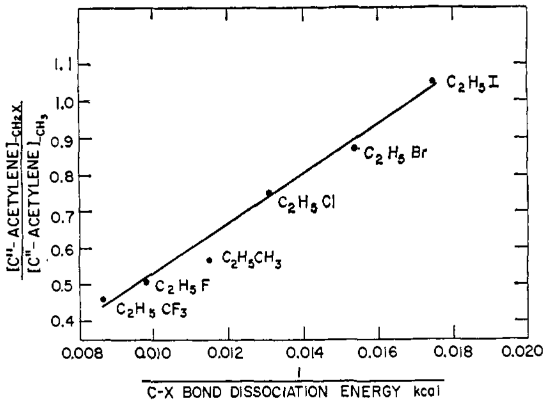

Figure 6. Correlation between acetylene yield ratios and bond dissociation energies.

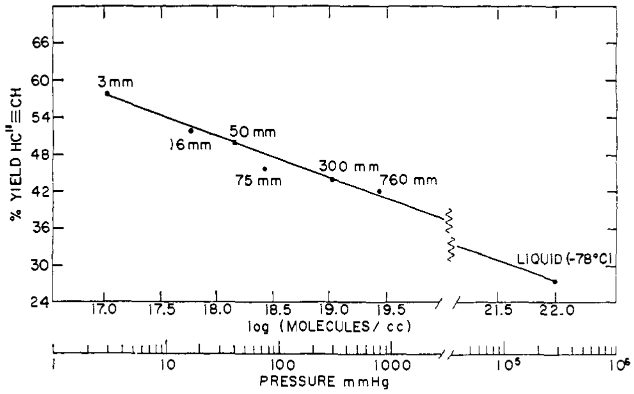

Figure 7. Pressure dependence of acetylene-$C^{11}$ yields from cyclopropane.

investigated the products from the reaction of methylene with isopropyl chloride and isopropyl bromide. The $\alpha$ hydrogen was less reactive than the $\beta$ hydrogens in both cases, and the $\alpha$ hydrogen on the bromide was less reactive than the $\alpha$ hydrogen on the chloride. Whether this was due to steric or electronic factors or both was not made clear in this work.

The increased acetylene-$C^{11}$ production from the methylene group could also be caused by an increase in the decomposition probability of the complex as the bond dissociation energies of the groups attached to the acetylene-$C^{11}$ forming moiety decrease. The ratios $[C_2H_2]_{CH_2X}/[C_2H_2]_{CH_3}$- are plotted *vs.* the reciprocals of the corresponding bond dissociation energies[30a,b] of the C–X bonds in Figure 6 for the five compounds studied. An additional point for propane (where X = $CH_3$) has been included. The fit for the series of halides is excellent as is the fit for the trifluoromethyl group. The point for propane which like the trifluoromethyl compound does not properly belong to this series can be seen to give a reasonable fit. This result provides strong support for the contention that the decomposition probability of the complex is dependent on the bond-dissociation energies of the bonds that need to be broken. In addition, it supports the view that these reactions occur at relatively low energies. This is consistent with earlier findings on the phase dependence of "hot" yields.[7] The fit for propane in Figure 5 could be due to the nature of the intermediate if a two-step mechanism is operative in the decomposition step, or it may simply be due to the greater difficulty in getting precise data for the partially deuterated propanes due to the nature of corrections that need to be made for the actual deuterium concentration in a particular "specifically" deuterated propane. Further evidence for the energy dependence of the decomposition step is provided by the striking pressure dependence of acetylene-$C^{11}$ yields from cyclopropane in an oxygen-scavenged system (Figure 7). The range of gas pressures was varied over a factor of 250 and a value for the liquid at −78° is also included.[31]

A detailed investigation of this pressure dependence should provide data on the energies at which this excitation–decomposition reaction is taking place.[32]

The absolute yield of acetylene from a particular molecule is related to a number of factors. The primary event depends on the collison probability per site. The question here is whether or not the carbon atom shows any selectivity in the collision event, and, if such selectivity exists, whether or not the site is capable of supporting intramolecular acetylene formation. The decomposition to acetylene may take place in a subsequent step in which the structural features and energy content of the complex affect the observed yield.[33] This paper has presented evidence bearing on the attack step and factors affecting the decomposition step.

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(30) (a) C. T. Mortimer, "Reaction Heats and Bond Strength," Pergamon Press, London, 1962; (b) T. L. Cottrell, "The Strength of Chemical Bonds," Academic Press Inc., New York, N. Y., 1954.

(31) A study of the photolytically produced cyclopropylcarbene ($C_4H_6$:) is being undertaken in order to provide a comparison with the hypothetical species produced in the carbon-11 atom reaction with cyclopropane.

(32) *Cf.* E. K. C. Lee and F. S. Rowland, *J. Am. Chem. Soc.*, **85**, 897 (1963), for pressure dependence studies in tritium hot-atom reactions.

(33) There is no *a priori* reason to assume that the acetylene-forming reactions are mechanistically identical in all their features as is obvious from the fact that benzene gives a 5% yield of acetylene when energetic carbon atoms are allowed to react with it. The simple mechanism suggested by eq 1 and 2 for the bulk of the acetylene cannot apply except possibly in the attack step.