of the standard as well as from those in other deposited films. The closest match in intensity is achieved in the deposits on Pyrex glass (entries nos. 2 and 4, Table II). One may assume little or no preferential orientation in these deposits. The deposition of Pt from (MeCp)PtMe$_3$, **1**, occurs at the lowest temperature (120 °C); these deposits show the greatest departure from the isotropic standard reflections. However, on the Si(100) surfaces there is preferred orientation; the most pronounced is seen in entry no. 5, with the Pt(200) being favored for the surface deposited films. By comparison, Pt films deposited in 3 min from Pt(ethylene)$_3$ at 50 °C in an ethylene stream (<1 atom % C) are amorphous.[27] The film resistivity for the Pt films was found to be around 26 $\mu\Omega$·cm. This value is somewhat higher than the film resistivity for Pt films derived from Pt(PF$_3$)$_4$ (18 $\mu\Omega$·cm),[4] and may be due to the lower temperature of deposition.

Analyses by X-ray photoelectron spectroscopy (XPS, Figure 9) shows no detectable amount of carbon (<1 atom % C) in the bulk of the film. These analyses are carried out after Ar$^+$ sputtering to remove the oxygen- and carbon-containing impurities on the surface. No other impurities are detected in the platinum. Scanning electron microscopy (SEM, Figure 8) shows smooth film composed of crystallites about 250 Å across compared with 1000 Å across in the Pt film from CpPtMe$_3$.[8]

Acknowledgment. This work was supported in part by a grant from the Raychem Corporation with a matching grant from the University of California Microelectronics Innovation and Computer Research Opportunities (MICRO) Program. We thank H. Thridandam and Dr. H.-J. Müller for permission to quote experimental results prior to publication. We also thank Dr. S. Khan for assistance with XRD studies, H. Thridandam and A. Lee for assistance with the SEM, Dr. Y.-J. Chen for helpful discussions, Yihui Yang and Professor J. S. Valentine for assistance with the UV spectra, and A. Owyeung for assitance with the illustrations.

Registry No. 1, 94442-22-5; MeCp, 26519-91-5; Me$_3$PtI, 14364-93-3; Pt, 7440-06-4.

Supplementary Material Available: ^{1}H homonuclear COSY contour plot of (MeCp)PtMe$_3$, **1** (Figure A), ^{1}H–^{13}C heteronuclear shift correlation contour plot of **1** (Figure B), diagram of the apparatus for the vapor pressure measurement (Figure C), UV spectrum of **1** in heptane (Figure D), least-squares plots of UV absorbance vs concentration of CpPtMe$_3$ and **1** (Figures E and F), comparison of melting points of (R-C$_5$H$_4$)$_n$ML$_x$ (R = H or Me) (Table A), final atomic parameters (Table B), selected bond distances and angles (Tables C and D), and final thermal parameters for the Pt atom (Table E) (8 pages); table of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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[27] Müller, H.-J.; Kaesz, H. D., manuscript in preparation.

Reactions of Carbon Atoms/Clusters with Methane, Methyl Bromide, and Water at 10 and 77 K

Gi Ho Jeong,[‡,1] **Kenneth J. Klabunde,**[*,‡] **Ohm-Guo Pan,**[†] **G. C. Paul,**[†] **and Philip B. Shevlin**[*,†]

Contribution from the Departments of Chemistry, Kansas State University, Manhattan, Kansas 66506, and Auburn University, Auburn, Alabama 36849. *Received April 3, 1989*

Abstract: The reactions of C atoms, C$_2$, and C$_3$ were monitored under matrix isolation conditions (10 K, argon) with methane, methyl bromide, and water. With CH$_4$ + C, the singlet state (^{1}D) reacted by C–H insertion followed by rearrangement to ethylene. Ground-state ^{3}P atoms did not react, although C$_2$ reacted but products could not be spectroscopically determined. Trimer C$_3$ and higher clusters did not react with CH$_4$. With CH$_3$Br, C, C$_2$, C$_3$, and higher clusters all reacted. The main product with C atoms was the stabilized carbene CH$_3$CBr formed by C–Br insertion. With H$_2$O, a major product was CO formed from ^{1}S and/or ^{1}D carbon atoms. Carbon clusters also reacted, but less efficiently than with CH$_3$Br. In order to determine the nature of the isolable products when carbon vapor reacted with methane, carbon arc experiments and 5-diazotetrazole decomposition experiments were carried out at 77 K. Isotope labeling and product analyses showed that C$_1$ reacted both by C–H insertion and hydrogen abstraction, and one mode for acetylene formation may be dimerization of CH. Vapor components C$_2$ and C$_3$ react with methane by hydrogen abstraction processes at 77 K.

Reactions of carbon atoms, dimers, and trimers have fascinated scientists for many years.[2] A variety of methods have been employed to generate carbon vapor, including arcs and thermal (resistive) heating. Differing portions of C versus C$_2$ versus C$_3$ are found with different evaporation methods.

The chemistry of C, C$_2$, and C$_3$ has been studied under a variety of conditions:[3] (a) simultaneous deposition of carbon vapor and reactant on a cold surface; (b) time-delay techniques, in which less than a monolayer of carbon is deposited onto an inert substrate and reactant added later; (c) gas-phase reactions (pyrolysis of reactant is a severe problem); and (d) lasers used to evaporate carbon in pulses; heating proceeds on a much shorter time scale.

Laser evaporation of carbon does provide some advantages.[4] A laser pulse can be very short, and the material evaporated can traverse the distance to the reaction zone (in this case a cold window) in the dark. During this time all excited state species will radiatively decay unless they are metastable states. Thus, in this work we evaporated carbon by focusing a XeCl excimer laser beam on a graphite rod. The experimental setup has been

Table I. Second-Order Rate Constants of C (^{3}P, ^{1}D) with Various Gases (k: cm^3 s^{-1} molecule^{-1})[a]

gas	C(^{3}P)	C(^{1}D)
NO	$7.3 \pm 2.2 \times 10^{-11}$	$4.7 \pm 1.3 \times 10^{-11}$
O$_2$	$3.3 \pm 1.5 \times 10^{-11}$	2.6×10^{-11}
CO	$6.3 \pm 2.7 \times 10^{-32}$	$1.6 \pm 0.6 \times 10^{-11}$
CH$_4$	$<2.5 \times 10^{-15}$	$2.1 \pm 0.5 \times 10^{-10}$
H$_2$O	$<3.6 \times 10^{-13}$	1.7×10^{-11}

[a] Data taken from ref 7.

[‡] Kansas State University.

[†] Auburn University.

[1] On leave from the Department of Chemistry, Busan National University, Busan, 609-735 South Korea.

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described earlier.[5] The vapor jet was cocondensed with argon and/or gaseous reactants on a cold KBr, KCl, or CaF_2 window. Reactant gases and argon were transparent to the 308-nm laser beam, so photolytic interactions should be minimal. Reactant pyrolysis problems are also eliminated using this method.

There are three low-lying energy states of the carbon atom: $C(^3P)$, $C(^1D)$, and $C(^1S)$. The ^1D state is 1.263 eV above the ground ^3P state, while the ^1S is 2.683 eV above the ground state. The ^1D metastable has a long lifetime while the ^1S is much shorter.[6] Because of the lifetimes of these metastable states, and the power of the laser beam, the generation of ^1S, ^1D, and ^3P carbon atoms is very likely, and they should survive the flight to the reaction zone. Thus, we must take into account reactivities of both singlet and triplet atoms.[7,8] Husain and Kirsch[7] have reported kinetic data on gas-phase carbon atom reactions with various molecules. The reaction rates were vastly different for ^3P versus ^1D. In particular, note that CH_4 and CO reacted much faster with ^1D (see Table I).

It has been predicted that the reaction of CH_4 with C atoms should proceed with a relatively low E_a.[9] Likewise, insertion of C into the O–H bond of H_2O has been predicted, through SCF calculations, to be a facile process, and H–C–OH should be bound with respect to C + H_2O by 50 kcal/mol.[10] Furthermore, trans H–C–OH has been predicted to be more stable than the cis isomer by 5–6 kcal. In another study, however, a rather large energy barrier to form H–C–OH has been predicted, and deoxygenation to generate CO + H_2 was proposed to be most favorable.[11] Indeed, recent experimental evidence and ab initio theoretical approaches allowed the conclusion that the process having the lowest E_a would be cleavage of an initially formed $C–OH_2$ adduct to CO + H_2.[12] However, formaldehyde could also form from a $C–OH_2$ adduct.

Other group 14 atoms (Si, Ge, Sn, and Pb) and their dimers form adducts with H_2O under matrix isolation conditions, and only insert into the O–H bond upon photolysis.[13] The M - OH_2 adduct was detected by a change in infrared bending frequencies.

Hence, questions arise as to what species will form at very low temperatures (matrix isolation conditions) when carbon atoms are codeposited with water: H–C–OH, CO, H_2, or $C–OH_2$? Infrared spectroscopy should be able to differentiate these species. Also, what will form with C + methane or C + alkyl halides? Since these systems have never been investigated under such low-temperature conditions, we believed such a study was worthwhile.

It must be pointed out though that the carbon vapor–argon system has been studied extensively by Weltner and co-workers.[14-16] This previous work was very helpful to us, especially for IR band assignments for carbon clusters (believed to be linear species).

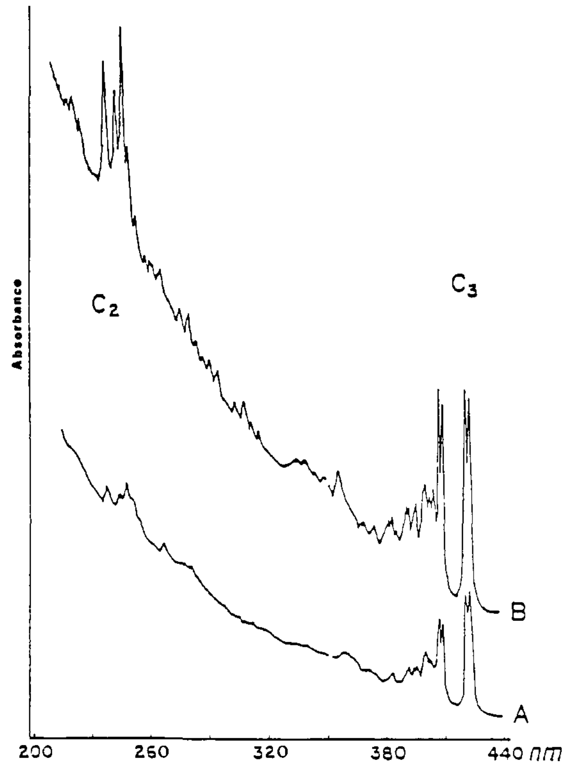

Figure 1. UV absorption spectra for C_2 and C_3 at 10 K: (A) in 5% CH_4/argon, laser evaporation time = 15 min (XeCl excimer laser, 75 mJ/pulse, 10 Hz); (B) in pure argon, evaporation time = 15 min (same laser conditions).

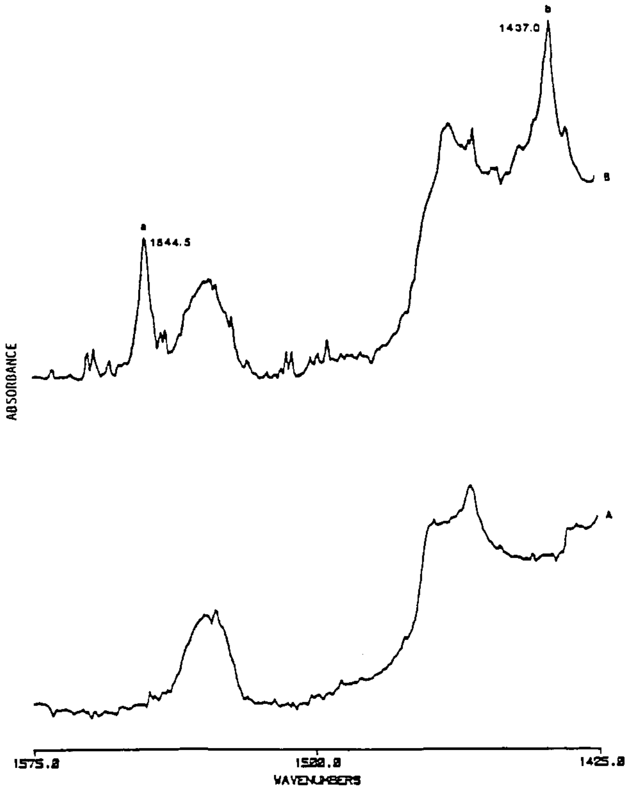

Figure 2. Partial infrared absorption spectra of carbon vapor/methane system at 10 K: (A) methane, (B) carbon plus methane.

Results and Discussion

Carbon and Methane. Laser-produced carbon vapor was trapped at 10 K in argon. Then UV-vis spectroscopy was used to monitor the matrix trapping of C_2 and C_3, as previously reported by Milligan and co-workers[17] and Weltner and co-workers.[14]

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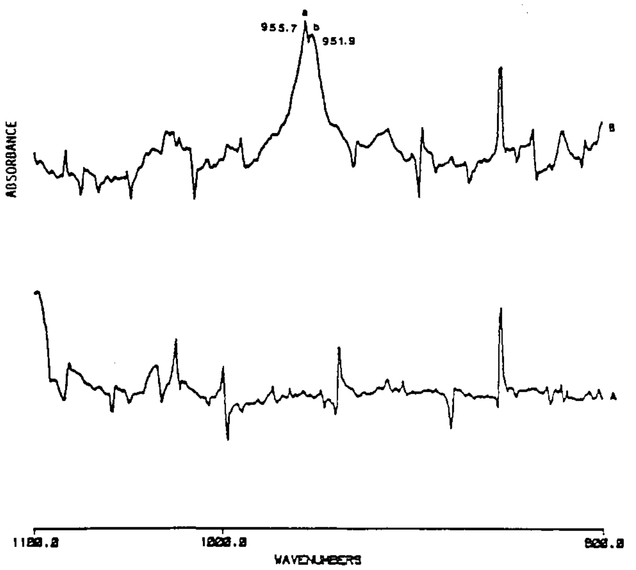


Figure 3. Partial infrared absorption spectra of carbon vapor/methane system at 10 K: (A) methane only, (B) carbon plus methane).

Unfortunately, carbon atoms could not be monitored since they absorb in the vacuum UV. Figure 1 shows a typical spectrum. The lower spectrum shows C_2 and C_3 deposited with 5% CH_4/Ar and the upper spectrum in pure Ar. Note that the band intensity for C_3 is slightly reduced while C_2 shows a much reduced intensity in the CH_4/Ar matrix. In *pure* CH_4, both C_2 and C_3 were completely consumed.

An FT-IR study of the carbon–methane system is illustrated in Figures 2–4. The new bands observed when carbon and methane were combined can be assigned to ethylene as the major product. Thus, the band at 1544.5 cm^{-1} can be assigned to $\nu_{C=C}$ (trapping in certain matrix sites could allow an asymmetry so that this band can be observed).[18] The 1437.0-cm^{-1} band can be assigned to CH_2 bending, and 955.7, 951.9 to $H_2C{=}CH$ deformation.[19]

Since earlier studies of gas-phase carbon species have shown that ^1D carbon atoms are much more reactive with CH_4 than ^3P,[7,8] and since our results show that C_2H_4 is readily formed, we believe this reaction product comes from ^1S or ^1D atoms (singlet-state atoms yielding singlet molecules):

$$C(^1D) + CH_4 \rightarrow H{-}C{-}CH_3 \rightarrow H_2C{=}CH_2$$

Another new feature observed in the carbon/CH_4 spectra is the significant reduction in C_3 (see band "b" in Figure 4) when pure CH_4 is present. Also note a band "a" in Figure 4 at 2136.6 cm^{-1}, which could be due to an acetylenic compound. It seems that C_3 reacts in a CH_4 matrix, but product identification from C_3 (or C_2) is difficult by matrix spectroscopy approaches (but see later discussion). This is unfortunate since C_3 is such an abundant species in the vapor.[20-22] However, the presence of a plethora of large carbon clusters, which appear to be unreactive in CH_4 and exhibit many active IR bands, makes spectroscopic product identification very difficult. (Figure 4 shows many of the IR bands due to clusters; assignments have been given by Weltner and co-workers.[15,23])

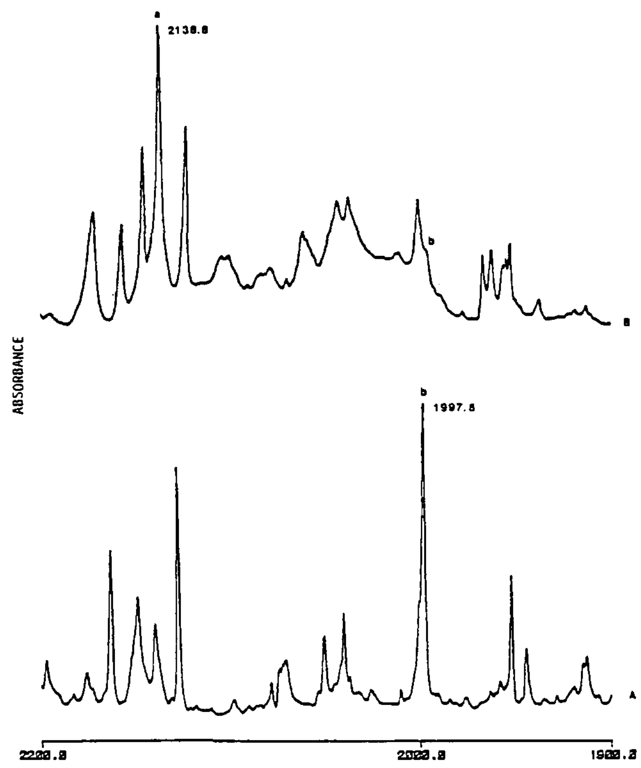
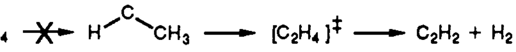


Figure 4. Partial infrared absorption spectra of carbon vapor/methane system at 10 K: (A) carbon in argon, (B) carbon in methane. Bands are mainly due to carbon clusters.

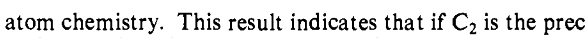
Since the matrix isolation studies presented such problems with product identification, larger scale reactions were undertaken at 77 K. A carbon arc was used first as the source of C_1, C_2, and C_3.[24] The products of these species reacting with methane as determined by GC, GC–MS, and IR are ethylene, acetylene, ethane, butadiyne, and trace amounts of allene (eq 1).

$$C_{(vapor)} + CH_4 \rightarrow C_2H_2 + C_2H_4 + C_2H_6 + CH_2{=}C{=}CH_2 + HC{\equiv}C{-}C{\equiv}CH \quad (1)$$

In order to obtain information concerning the mechanism of the formation of the acetylene, allene, and butadiyne, we have condensed carbon vapor at 77 K in the presence of a mixture of CH_4 and CD_4 (1.23:1) and have examined the label distribution in these products by mass spectrometry. The acetylene generated in this reaction was in the ratio d_0:d_1:d_2 = 1:2.08:1.06. This type of deuterium distribution rules out any substantial contribution to the mechanism of acetylene formation by decomposition of energetic ethanylidene (eq 2) or ethylene (eq 3), processes which may be important at low pressures in the gas phase and in hot



$$C + CH_4 \not\rightarrow [H{-}\overset{\cdot\cdot}{C}{-}CH_3]^{\ddagger} \longrightarrow C_2H_2 + H_2 \quad (2)$$



$$C + CH_4 \not\rightarrow H{-}\overset{\cdot\cdot}{C}{-}CH_3 \longrightarrow [C_2H_4]^{\ddagger} \longrightarrow C_2H_2 + H_2 \quad (3)$$

atom chemistry. This result indicates that if C_2 is the precursor to the acetylene, it removes hydrogen from two separate methane molecules in a series of consecutive abstractions (eq 4). (We

$$C{\equiv}C + CH_4 \rightarrow H{-}C{\equiv}C \xrightarrow{CH_4} H{-}C{\equiv}C{-}H \quad (4)$$

believe our system is free of residual hydrogen, thus ruling out acetylene formation from $C_2 + H_2$.) However, another mechanism for acetylene formation in this system consistent with the label distribution is initial abstraction of H from methane to generate

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methylidyne (CH) which subsequently dimerizes (eq 5). It has

$$C + CH_4 \rightarrow H{-}C \xrightarrow{H-C} H{-}C{\equiv}C{-}H \qquad (5)$$

been demonstrated that arc-generated C atoms abstract hydrogen from benzene[25] to give CH, and it may be that this mechanism is operative in this system as well. Consideration of the ratios of labeled products along with the ratio of starting methanes leads to the conclusion that there is an inverse isotope effect ($k_H/k_D = 0.79$) on the hydrogen abstraction. While the origin of this isotope effect is not clear, it is interesting that abstraction of H or D from C_2H_6/C_2D_6 by ^{11}C atoms has a $k_H/k_D = 0.83$ at room temperature.[26]

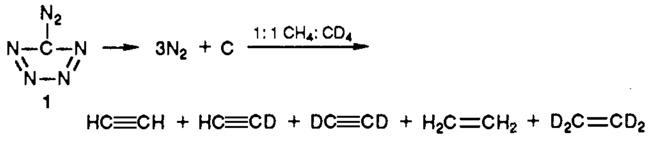
Since acetylene formation in this system involves a small inverse isotope effect, it is instructive to examine the label distribution in the 1,3-butadiyne generated in this reaction. In this case, d_0:d_1:d_2 = 1:0.24:1.5 × 10^{-3}, and the results are consistent with a substantial normal deuterium isotope effect in striking contrast to the acetylene case. It is thus clear that the butadiyne and the acetylene cannot arise from hydrogen abstractions by the same species. Possible mechanisms of formation of 1,3-butadiyne include dimerization of C_2H (eq 6) and consecutive H abstractions by C_4 (eq 7). An examination of the ratio of butadiyne-d_0 to

$$\bullet C{\equiv}C\bullet + CH_4 \rightarrow H{-}C{\equiv}C\bullet \xrightarrow{H-C\equiv C\bullet} H{-}C{\equiv}C{-}C{\equiv}C{-}H \qquad (6)$$

$$\bullet C{\equiv}C{-}C{\equiv}C\bullet + CH_4 \rightarrow H{-}C{\equiv}C{-}C{\equiv}C\bullet \xrightarrow{CH_4} H{-}C{\equiv}C{-}C{\equiv}C{-}H \qquad (7)$$

-d_1 indicates an isotope effect of k_H/k_D of 6.8 for the hydrogen abstractions leading to this species. Since the acetylene and butadiyne show substantially different isotope effects on their formation, they both cannot have C_2H as a precursor.

In order to clarify the mechanism of acetylene formation in the reaction of carbon with methane, we have generated C_1 by the decomposition of 5-diazotetrazole (**1**)[27] in the presence of gaseous methane. When **1** was decomposed in the presence of a mixture of CH_4 and CD_4, the reaction was complicated by the fact that some C_2H_2 was generated in a concerted decomposition of a tetrazole dimer formed during the production of **1**. However, the ratio of C_2HD to C_2D_2 indicates that the acetylene is again statistically labeled with a small isotope effect favoring D abstraction (k_H/k_D = 0.90, 110 °C) in the same manner as that produced in the reaction of arc-generated C vapor with methane. Since the decomposition of **1** in the presence a large excess of methane is unlikely to generate C_2, *we feel that dimerization of CH (eq 5) is the most reasonable mechanism of acetylene formation in this system.* If we take the small inverse isotope effect on acetylene formation under both sets of reaction conditions as evidence that the same mechanism is operative in both cases, we conclude that the majority of acetylene formed in the reaction of C vapor with CH_4 results from dimerization of CH.



If the butadiyne results from dimerization of C_2H, a reaction which has been shown to be extremely rapid,[28] the observed isotope effect is for the abstraction of hydrogen from methane by C_2. Although the isotope effect on abstractions by either C or C_2 on methane has not been measured, the corresponding reactions of both of these intermediates with H_2 and D_2 have been investigated. The reaction of C(^{1}D) with H_2 to generate CH (eq 8) proceeds without isotope effect,[29] while the abstraction of hydrogen from H_2 or D_2 by $^3C_2$ (eq 9) has a k_H/k_D = 5.2 at 350 K.[30] Since the

$$C + H_2 \rightarrow H{-}C \qquad k_H/k_D = 1 \qquad (8)$$

$$\bullet C{\equiv}C\bullet + H_2 \rightarrow H{-}C{\equiv}C\bullet \qquad k_H/k_D = 5.2 \qquad (9)$$

reaction of $^3C_2$ with H_2 ($A = 1.55 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, E_a = 3.01 kcal/mol)[30] should be similar to that of $^3C_2$ with CH_4 ($A = 1.65 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, E_a = 5.57 kcal/mol),[31] we conclude that an isotope effect on H abstraction by $^3C_2$ is expected. The most likely reaction between $^3C_2$ and methane is hydrogen abstraction to give C_2H.[32] This species would subsequently dimerize to butadiyne. Although these results do not rule out a mechanism for butadiyne formation involving sequential H abstractions by C_4 upon which there is a k_H/k_D = 6.8, the amount of C_4 in arc generated carbon vapor has been shown to be relatively low.[2]

The products reported here for the condensation of carbon vapor with methane at 77 K indicate that both C–H insertion and hydrogen abstraction occur with C while H abstractions probably dominate in the reactions of C_2 and C_3. If this is the case, we may expect to find spectral evidence for some of these hydrogen abstraction products in the low-temperature matrix experiments. Ethynyl radical, C_2H, the initial product of hydrogen abstraction by C_2, has been observed to show a carbon–carbon stretch at 1848 cm^{-1} in a Kr matrix at 12 K.[33] Propynylidyne, C_3H, and propynylidene, HC≡C—CH, the respective products of abstraction of one of two hydrogens by C_3, have been shown to absorb at 1834 and 2140 cm^{-1} in Kr matrices at 12 K.[33] Returning to our matrix isolation studies, one band is indeed present in these regions. Thus, the 2136.6-cm^{-1} band could be due to HC≡C—CH; (bands for C_2H were not observed). Since C_3 was partially consumed by pure CH_4, the formation of some HC≡C—CH does seem probable. Still another possibility is the C_3H_2 isomer H_2C=C=C:, vinylidenecarbene. Maier and co-workers[34] report IR bands at 1963, 1952, and 1000 cm^{-1}, and we observe new bands in these regions. Thus, it appears that C_3H_2 (at least two isomers) is formed in the C_3/CH_4 reaction under low-temperature conditions.

An examination of the deuterium distribution in the allene produced in the reaction of arc generated carbon vapor with the 1.23:1 mixture of CH_4 and CD_4 revealed a ratio of d_0:d_1:d_2:d_3:d_4 = 0.5:4.9:6.0:3.3:0.7. This ratio is close to the statistical 1.5:4.9:6.0:3.3:0.7 calculated for a series of H abstractions by C_3 on a 1.23:1 mixture of CH_4 and CD_4 with k_H/k_D = 1.

Analysis of the deuterium distribution in the ethylene generated in the condensation of carbon vapor with CH_4–CD_4 was not possible owing to incomplete separation from ethane in the GC–MS. However, the reaction of chemically generated C atoms, from decomposition of **1**, with 1.23:1 CH_4–CD_4 in the gas phase gave only C_2H_4 and C_2D_4, a result consistent with C–H insertion by C(^{1}D) to give ethanylidene which rearranged to ethylene. It is interesting that this reaction appears to be characterized by a normal primary isotope effect of 3.56.

Carbon and Methyl Bromide. Carbon vapor reacts efficiently with alkyl halides near 77 K, as previously shown by Skell and co-workers.[35] We were interested in finding out if such reactions proceeded at lower temperatures. Figure 5 illustrates that both C_2 and C_3 were almost completely consumed by 5% CH_3Br/Ar at near 10 K. Infrared studies (Figures 6–8) showed that larger carbon clusters were also consumed by CH_3Br, and several product bands were observed (Table II). First of all, Figure 7 shows

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Table II. Proposed Products and Their FT-IR Bands from the Carbon Vapor/CH_4, CH_3Br, and /H_2O Systems (cm^{-1}) at 10 K in Frozen Argon

proposed species			
C_2H_4 (from CH_4)	1544.5 $\nu_{C=C}$	1437.0 δ CH_2	955.7 951.9 def $H_2C=CH$
CH_3CBr (from CH_3Br)		746.5 (methyl sym bending)	1193.7 1095.1 (methyl asym bend)
CO (from H_2O)	2148.7, 2138 $\nu_{C=O}$		
acetylenic compds (from H_2O)		2051.8, 2038.3 $\nu_{C\equiv C}$	
CO (from D_2O)	2148 $\nu_{C=O}$		

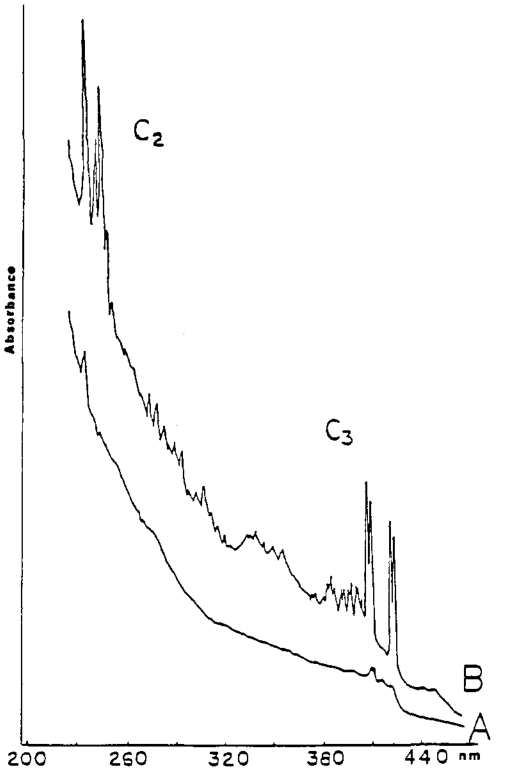

Figure 5. UV absorption spectra for C_2 and C_3 at 10 K in (A) 5% CH_3Br/argon, laser evaporation time = 20 min (XeCl excimer laser, 75 mJ/pulse, 10 Hz); (B) in pure argon, evaporation time = 20 min (same laser conditions).

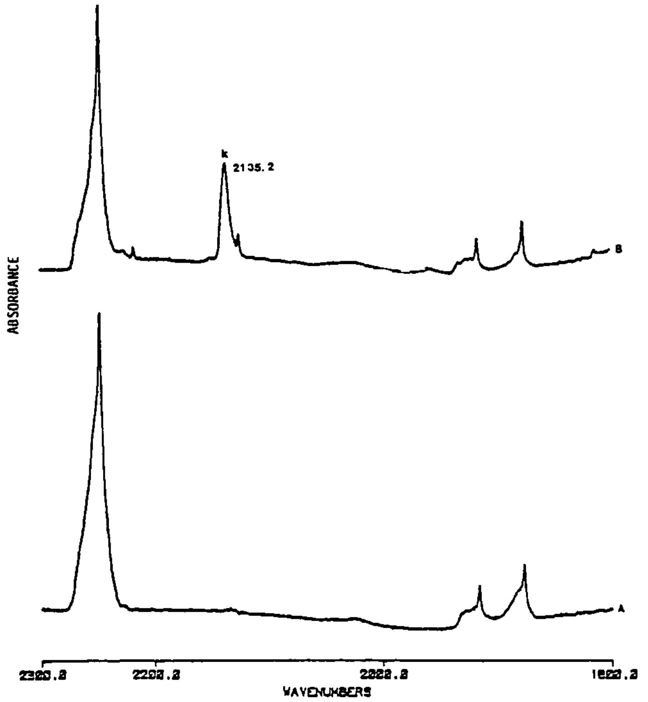

Figure 6. Partial infrared absorption spectra of carbon vapor/CH_3Br system at 10 K: (A) CH_3Br only, (B) carbon plus CH_3Br.

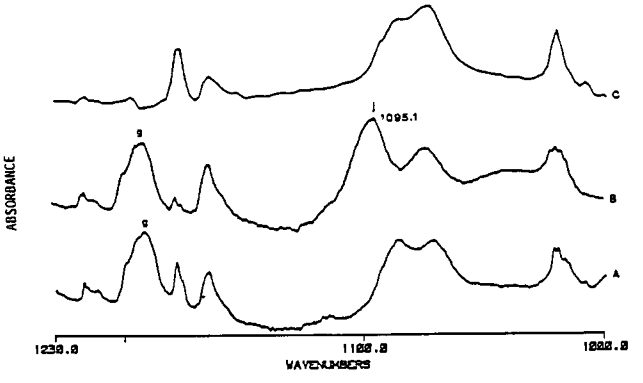

Figure 7. Partial infrared absorption spectra of carbon vapor/CH_3Br system: (A) carbon plus CH_3Br at 77 K; (B) carbon plus CH_3Br at 10 K, (C) CH_3Br only at 10 K.

spectra taken at 77 and 10 K. In both spectra a new band "g" at 1193 cm^{-1} was observed; a peak at this position could be due to an asymmetric CH_3 bending mode.[5,35] Also a new band at 746 cm^{-1} is probably due to a symmetric CH_3 bending mode. Another band at 1095 cm^{-1} is observed at 10 K and also could be due to a CH_3 bending mode. Becuase of the similarities with other CH_3-M-X systems we have seen in matrices before, it seems likely that a CH_3 derivative was present. Possibly the insertion product CH_3CBr was stabilized under these conditions. We did not observe bands assignable to $CH_2=CHBr$, although CH_3Br did obscure the $\nu_{C=C}$ region somewhat.

As with the CH_4 system, CH_3Br with carbon vapor yielded a strong band at 2135 cm^{-1}. This could be due to an acetylenic compound, perhaps $HC\equiv CCH$ resulting from hydrogen abstraction by C_3. Note that C_2, C_3, and larger carbon clusters were consumed by CH_3Br.

Based on the evidence at hand, and comparing with our boron atom/CH_3Br work, we believe carbon atoms reacted near 10 K to form the intermediate carbene. Since this is different from the

$$C + CH_3Br \rightarrow CH_3CBr$$

C/CH_4 system, where insertion was followed by rearrangement to C_2H_4, it seems likely that the upper electronic states of C atoms (^1S and ^1D) were quickly quenched by CH_3Br. Possibly only the ^3P state was available then, which did react, but the reaction stopped at the carbene stage. At higher temperatures, of course, rearrangements to stable products would take place.[35]

Carbon and Water. Using UV-vis spectroscopy to again monitor C_2 and C_3 consumption, we found that C_2 and C_3 interacted with water less efficiently than with CH_3Br, but more efficiently than with CH_4, as shown in Figure 9.

Infrared analyses (Figures 10–12) showed that carbon vapor deposited with H_2O/Ar did not yield bands that could be attributed to a simple adduct, which should show a change in the

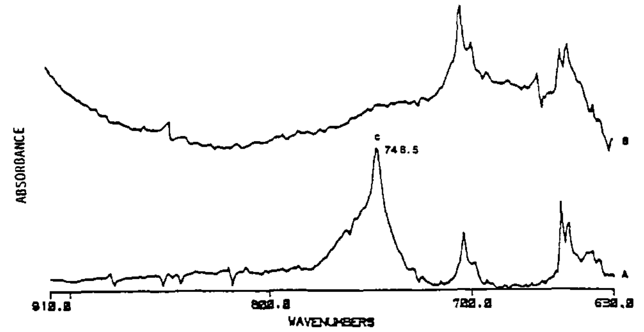

Figure 8. Partial infrared absorption spectra of carbon vapor/CH_3Br system at 10 K: (A) carbon plus CH_3Br, (B) CH_3Br only.

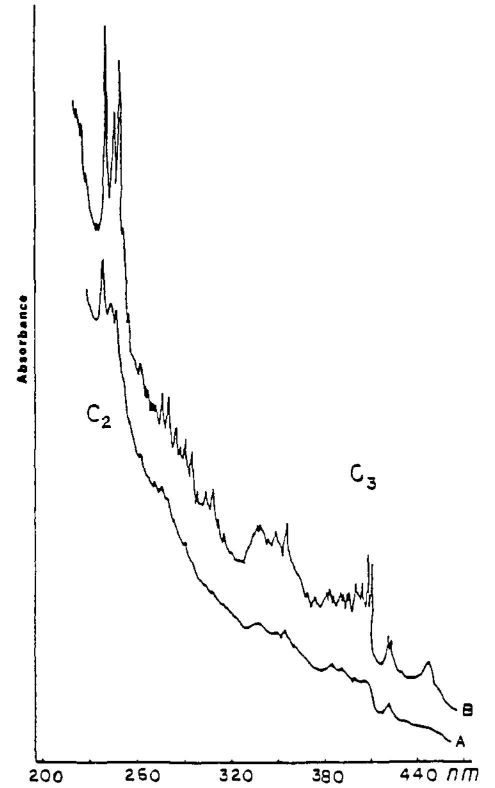

Figure 9. UV absorption spectra for C_2 and C_3 at 10 K: (A) in 10% H_2O/argon, laser evaporation time = 15 min (XeCl excimer laser, 75 mJ/pulse, 10 Hz); (B) in pure argon, laser evaporation time = 15 min (same laser conditions).

H_2O bending mode near 1600 cm^{-1} (Figure 12). Also, no new bands in the 1400-cm^{-1} region were observed (Figure 11), where ν_{C-O} might be expected for H–C–OH.[10] This is particularly interesting since such bands were predicted at 1335, 1375, and 1450 cm^{-1}.[10] On the other hand, our work with B/H_2O did show a band for ν_{B-O} in the predicted region for H–B–OH.[10,36]

Product bands that were found are illustrated on Figure 10. The "c" and "d" bands are probably due to $\nu_{C\equiv C}$ for products formed from C_2 and/or C_3 reactions with H_2O (perhaps C_3O or HC≡CCHO), but we are unable to assign structures at this time.

It can be seen that the C_3 band at 1997.8 cm^{-1} is greatly diminished in the presence of H_2O, supporting this idea. Note, however, that these product bands were not observed in the analogous C/D_2O experiments. (Figure 10 C). Since deuterium shifted bands were not observed, we can only conclude that a large isotope effect must have prevented these analogous reactions with D_2O under these low-temperature conditions. In support of this, notice, the continued presence of the C_3 band. It should also be

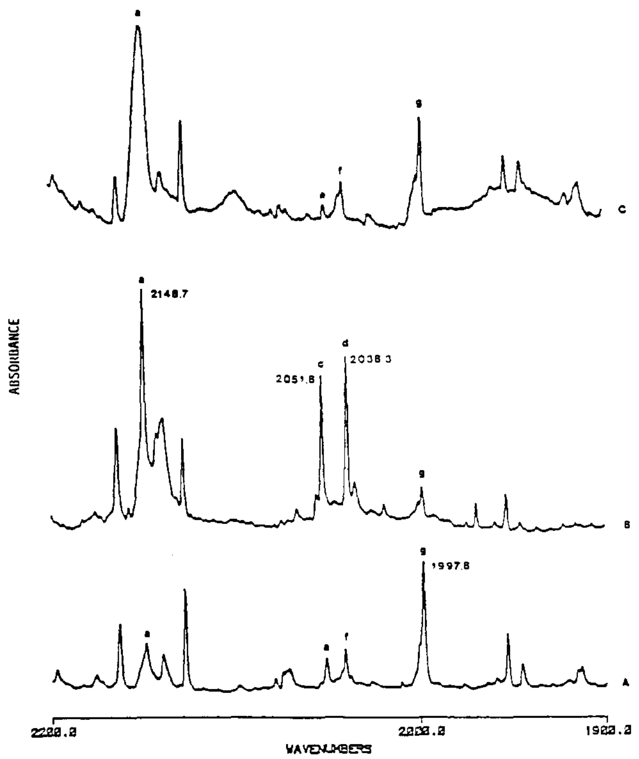

Figure 10. Partial infrared absorption spectra of carbon vapor/H_2O system at 10 K: (A) carbon in argon, (B) carbon plus 1% H_2O/argon, (C) carbon plus 1% D_2O/argon.

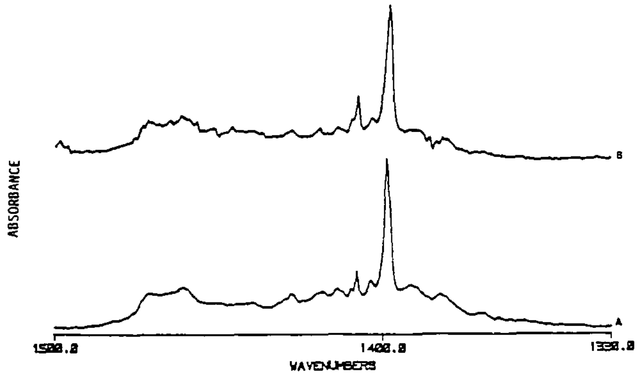

Figure 11. Partial infrared absorption spectra of carbon vapor/H_2O system at 10 K: (A) 1% H_2O in argon, (B) carbon plus 1% H_2O in argon.

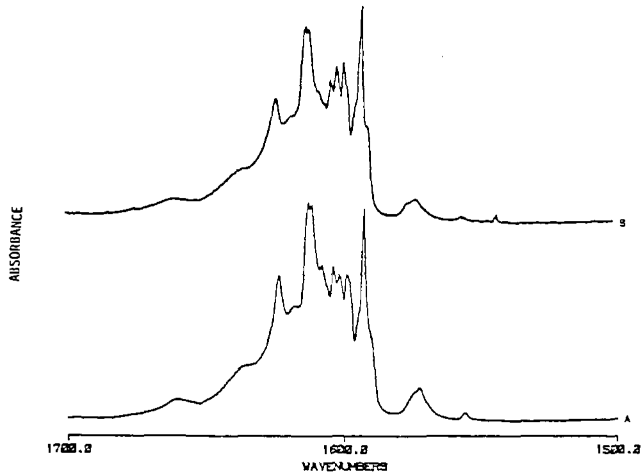

Figure 12. Partial infrared absorption spectra of carbon vapor/H_2O system at 10 K: (A) 1% H_2O in argon, (B) carbon plus 1% H_2O in argon.

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noted that IR bands from larger carbon clusters still remained even in the presence of H_2O/Ar or D_2O/Ar.

The most prominent product band appeared at 2148.7 cm^{-1}, and we believe this is due to CO. A broader band at 2138 was also observed with C/H_2O, but with C/D_2O a much broader band centered at 2148 was observed.

Several workers have examined CO in frozen argon and have observed two bands.[18,37] Pimentel and co-workers[38] reported that the 2148 band is due to monomeric CO while the 2138 band is due to aggregates of CO, with the higher energy band exhibiting an expected narrower line width. Pure, frozen CO shows a broad band centered at 2138 cm^{-1}.[18,37,39]

We conclude that carbon atoms, probably ^1D, reacted with H_2O to form CO + H_2 under our experimental conditions (near 10 K and 1% H_2O in argon). We do not find any evidence for formaldehyde, adduct C–OH_2, or a stabilized insertion product H–C–OH. This contrasts with B atoms, which do yield an insertion product H–B–OH.[36] Note, however, that reaction of C(^1D) with H_2O at 100 °C generates CO and $CH_2{=}O$ in a 4:1 ratio.[12] If the *A* factor for CO formation is greater than or equal to the *A* factor for $CH_2{=}O$ formation, the CO:$CH_2{=}O$ ratio would be ≥28.6 at 10 K. This small amount of $CH_2{=}O$ would probably be undetectable in our system (matrix isolation conditions).

Conclusions

To summarize our carbon vapor/CH_4 results, we conclude that (1) C(^1S and ^1D) reacted near 10 and 77 K by carbon–hydrogen insertion and rearrangement to ethylene. Another reaction mode, perhaps with C(^3P) was hydrogen abstraction to yield CH which subsequently dimerized to form acetylene. (2) C_2 and C_3 reacted by hydrogen abstraction processes, and the matrix isolation studies revealed IR absorption that could be due to intermediate $HC{\equiv}CCH$ and $H_2C{=}C{=}C{:}$. (3) Butadiyne was formed by dimerization of C_2H through hydrogen abstraction by C_2. (4) Larger carbon clusters were relatively unreactive with methane near 10 K.

With CH_3Br carbon atoms reacted, and the evidence suggests that the insertion product CH_3CBr carbene was trapped at 10 K. This product is probably the result of reaction C(^3P), and C(^1S and ^1D) atoms seem to be quenched rapidly in the presence of CH_3Br. Carbon clusters also reacted, but products could not be determined. However, a band that could be due to $HC{\equiv}CCH$ was observed which could come from hydrogen abstraction by C_3.

With water, carbon atoms reacted, probably C(^1D), to yield CO and, presumably, hydrogen. No evidence for a simple adduct C–OH_2, and insertion product HCOH, or formaldehyde was found at 10 K. Carbon clusters reacted with water to yield acetylenic products that could not be identified as yet. However, D_2O reacted much less efficiently than H_2O.

Experimental Section

Matrix Isolation Experiments at 10 K. Vapors of carbon were generated by focusing a XeCl excimer laser (Questek Series 2000) beam on the target surface positioned in the vacuum chamber.[5] A large excess of prepurified argon gas containing the reactive species (such as CH_4, CH_3Br, or H_2O) was supplied from an outside bulb. These were cocondensed on the CaF_2 window for UV–vis absorption experiments, or on KBr for infrared absorption experiments. The temperature of the window was kept at 10 K by an Air Products Displex closed-cycle helium refrigerator. The pressure of the reaction chamber was kept near 1×10^{-5} Torr. Laser pulses continued for about 10 min for UV–vis absorption studies and for 2–3 h for infrared absorption studies.

The prepurified Ar (99.995%), ultrahigh-purity CH_4 (99.73%), and high-purity CH_3Br (99.5%) were supplied by Matheson Gas Products. Ar and CH_4 were passed through a liquid N_2 trap before storing in the glass bulb. CH_4 and CH_3Br were used in pure form for the infrared absorption studies. For the UV–vis absorption studies, in order to compare the band areas in solid argon with those in CH_4 or CH_3Br, the reagents were diluted in argon. The concentration of reactants CH_4, CH_3Br, or H_2O in Ar was 5 or 1% as desired. Water was mixed with argon both for UV–vis and infrared absorption studies. Carbon rods were obtained from Johnson Matthey. CD_4 (99% D) and CD_3Br (99.5% D) were supplied from ICN Biochemicals, and D_2O (99.75% D) was obtained from J. T. Baker. Water was placed in a small tube which was connected to the main bulb through a valve. Before mixing water with the argon, the water was degassed to remove dissolved oxygen. Starting with a sample of doubly distilled and deionized water, a series of pumping–freezing cycles was initiated. The sample was frozen and opened to vacuum, with pumping continued while thawing. This freezing–thawing–pumping cycle was repeated five times for a given sample. The sample was then warmed again to room temperature and partially evaporated under vacuum to ensure complete degassing for half an hour before mixing. The UV–vis atomic absorption spectrum was taken in both matrices (pure argon and mixed matrix) to compare band areas.

The UV–vis absorption spectra were taken on a Cary-14 spectrophotometer with a resolution of 1 nm. Reaction products were investigated by infrared absorption using a DigiLab FTS/40 Fourier transform infrared spectrometer with a resolution of 1 cm^{-1}. Laser-generated carbon vapor was cocondensed with CH_4, CH_3Br, or H_2O on a KBr window in the vacuum chamber at 10 K.

A schematic diagram of a reaction chamber has been reported earlier.[5] After passing through a concave lens (*f*/6 in.), the focused laser beam (75 to 140 mJ/pulse and about 5 pulses/s) was directed through the cold trapping window (a hole in the window) onto the target, which was vaporized. The vapor is directed back along the laser beam path and onto the window.[40,41]

Reactions of Arc-Generated Carbon Vapor with Methane. The reactor design has been reported by Skell, Wescott, Goldstein, and Engel.[24] Carbon was vaporized by striking an intermittent arc between two graphite rods attached to water-cooled brass electrodes and condensed on the walls of the reactor at 77 K with reactants under vacuum. In a typical reaction, methane (140 mmol) was introduced into the reactor through the vacuum line and cocondensed on the walls of the reactor at 77 K with carbon vapor (118 mmol). After the reaction, the volatiles were pumped into a trap at 77 K. The volatile contents of the trap were analyzed by IR spectroscopy and quantitated by GC/MS (6 ft Porapak Q column). Products identified were acetylene (4.25 mmol), ethylene (1.53 mmol), ethane (2.72 mmol), butadiyne ().83 mmol), and trace amounts of allene which was detected in the IR and GC/MS in amounts too small to be quantitated.

Reaction of Arc-Generated Carbon Vapor with a Mixture of CH_4 and CD_4. This reaction was carried out as described above using a 1.23:1 mixture of CH_4–CD_4. The products were analyzed by GC/MS, and the deuterium distribution in the acetylene, butadiene, and allene was determined from the mass spectrum. The inability to separate ethane and ethylene by GC prevented an analysis of their deuterium distribution.

Decomposition of 5-Diazotetrazole (1), in the Presence of CD_4–CD_4. The diazotetrazole **1** was prepared from 1 g of 5-aminotetrazole and coated on the walls of a 500-mL round-bottom flask as previously described.[42] The flask containing **1** was evacuated, and 100 mm of a mixture of CH_4–CD_4 (1.23:1) was introduced. The diazotetrazole was decomposed by heating at 110 °C for 5 min. At the conclusion of the reaction, volatiles were pumped through traps at −78 and −196 °C. The contents of the −196° trap were analyzed by IR spectroscopy which showed C_2H_4 (14.0×10^{-4} mmol), C_2D_4 (3.2×10^{-4} mmol), C_2H_2 (7.0×10^{-4} mmol), C_2HD (2.0×10^{-4} mmol), and C_2D_2 (0.9×10^{-4} mmol). Pyrolysis of **1** in the absence of substrate revealed considerable amounts of C_2H_2 which is thought to result from decomposition of a dimer formed during the diazotization process.[43]

Acknowledgment. The support of the National Science Foundation is acknowledged with gratitude.

Registry No. 1, 86457-85-4; C, 7440-44-0; C_2, 12070-15-4; C_3, 12075-35-3; CH_4, 74-82-8; CH_3Br, 74-83-9; H_2O, 7732-18-5; D_2, 7782-39-0.

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(41) Kang, H., and Beachamp, J. L. (*J. Phys. Chem.* **1985**, *89*, 3364–3367), have demonstrated that the vapor preferentially exits directly back along the laser beam path. This is because a hole is bored, acting like a rifle barrel directing the beam. This gives another advantage in that very little surface oxide is encountered by the beam, and so oxide vapor contaminents are minimized.

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