Evidence for the Electronic States of Recoil Carbon Atoms Undergoing Reaction[1a]

Kathleen K. Taylor,[1b] Hans J. Ache,[1b] and Alfred P. Wolf*[1c]

Contribution from the Chemistry Departments, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, and the Brookhaven National Laboratory, Upton, New York 11973. *Received February 9, 1976*

Abstract: The electronic states of carbon responsible for product formation in systems where the carbon atom is generated by nuclear transformation have been investigated using noble gases in admixture with oxygen-scavenged ethane. Variations in the yields of ethylene-^{11}C, acetylene-^{11}C, and carbon-^{11}C monoxide with increasing xenon concentration are explained on the basis of intersystem crossing from ^1D to ^3P carbon. These results are compared to those in helium and neon, where energy degradation is an efficient process, but spin conversion is expected to be unimportant. Acetylene-^{11}C is attributed to reaction by high-energy $C(^3P)$ and low-energy $C(^1D)$, whereas ethylene-^{11}C is formed essentially by high-energy $C(^1D)$. Low-energy $C(^3P)$ is efficiently scavenged by oxygen to form carbon-^{11}C monoxide. Near thermal $C(^3P)$ may also undergo C–H insertion to lead to labeled products as a minor pathway.

The hot atom chemistry of carbon has been extensively studied and general mechanisms for its reactions with hydrocarbons have been proposed.[2,3] However, very little is known about how the reactivity of the hot carbon atom is altered by changing its electronic spin state. This is an important consideration in hot systems, where the presence of several states separated from the ground state by spin forbidden transitions is a certainty. The carbon atom has three states which may play a role in recoil reactions, $C(^1D)$ at 1.26 eV and $C(^1S)$ at 2.68 eV above the $C(^3P)$ ground state.[4] We describe here experiments using noble gases to determine the relative importance of these spin states in product formation.

Experimental Section

Ethane containing 4.5% oxygen scavenger was chosen as the substrate and mixtures were prepared containing 0, 0.5, 0.7, 0.9, 0.95, and 0.98 mole fraction xenon or neon at a constant total pressure of 700 mmHg. These data were compared to previously published data in helium.[5] In all samples the ethane-oxygen ratio was maintained constant at 21:1. The gas mixtures were contained in quartz vessels and subjected to a diffused beam of 33-MeV protons at the BNL 60-in. cyclotron to produce free carbon atoms by the $^{12}C(p,pn)^{11}C$ reaction.[6] All samples were irradiated for 50 s at a 1-μA beam intensity, producing an absorbed dose of approximately 7×10^{-3} eV/molecule as determined by acetylene-to-benzene dosimetry.[7,8] Products were identified by gas chromatography and monitored by a window proportional counter.[9] In the case of xenon, total activity produced was measured by converting all carbon compounds to CO_2 in a furnace containing excess oxygen at 700 °C. The resulting carbon dioxide was quantitatively absorbed on Ascarite and counted as such using a well-type NaI(Tl) scintillator. This procedure avoided the problem of radioactive contamination by other isotopes formed during the bombardment.

Results and Discussion

Figure 1 shows the trend of the yields of the major products with increasing mole fraction of xenon. As is generally true with oxygen-scavenged acyclic alkanes, acetylene-^{11}C, ethylene-^{11}C, and carbon-^{11}C monoxide account for well over 50% of the total activity produced in the gas phase. Carbon-^{11}C monoxide has been demonstrated to be the result of scavenging of thermalized carbon atoms by oxygen molecules.[10,11] Confirmation was provided by the work of Braun et al.[12] and Husain and Kirsch,[13] who photolyzed carbon suboxide in the presence of added gases and measured the rate of disappearance of $C(^3P)$. All groups reported the rate of disappearance in oxygen to be four orders of magnitude faster than with hydrocarbons. It was found that $C(^1D)$ disappeared at similar rates in both oxygen and hydrocarbons and at a rate comparable to $C(^3P)$ loss in oxygen. The oxygen content of our systems is limited to 4.5% of the alkane-oxygen mixture in order to ensure that any carbon atoms encountering oxygen molecules will have undergone a sufficient number of collisions in order to reach thermal energies. Any $C(^1D)$ reaching this energy range will have a higher probability of reaction with the hydrocarbon than with oxygen. Therefore, the major species contributing to carbon monoxide must be $C(^3P)$.

The mechanisms by which acetylene-^{11}C and ethylene-^{11}C are produced have been of primary importance in delineating the reactions of hot carbon atoms. It is now generally agreed[14,15] that in saturated compounds acetylene-^{11}C is primarily the result of insertion by an energetic carbon atom into the C–H bond of a hydrocarbon, followed by unimolecular decomposition of the excited intermediate (eq 1 and 2). The weight of evidence[16] indicates that ethylene-^{11}C is produced via a methyne-^{11}C intermediate which inserts into a methyl C–H bond. Decomposition of the resulting intermediate gives ethylene-^{11}C directly (eq 1, 3-5).

$$RCH_3 + {}^{11}C \longrightarrow RCH_2{}^{11}CH \quad (1)$$

$$RCH_2{}^{11}CH \longrightarrow \begin{cases} \text{other products} \\ HC{\equiv}{}^{11}CH + R + H \end{cases} \quad (2)$$

$$RCH_3 + {}^{11}C \longrightarrow RCH_2{}^{11}CH \quad (1)$$

$$RCH_2{}^{11}CH \longrightarrow \begin{cases} \text{other products} \\ RCH_2 + {}^{11}CH \end{cases} \quad (3)$$

$${}^{11}CH + RCH_3 \longrightarrow RCH_2{}^{11}CH_2 \quad (4)$$

$$RCH_2{}^{11}CH_2 \longrightarrow R + CH_2{=}{}^{11}CH_2 \quad (5)$$

Various workers[4,17] have attempted to assign products to specific states of the carbon atom. Starting with Massey and Burhop's resonance rule[18] for estimating cross sections for energy changing processes, Marshall et al.[17] concluded that only $C(^3P)$, $C(^1D)$, and $C(^1S)$ would be expected to survive to the chemical energy range. Skell[19] reported the observation of $C(^1S)$ based on precursor lifetimes in his carbon arc studies; and Meaburn and Perner[20] measured the rate of disappearance of $C(^1S)$ following pulse radiolysis. However, $C(^1S)$ has generally been excluded[21] from further consideration in hot atom systems due to the additional 33 kcal of energy which it carries into reaction. Recent evidence based on calculations by Blint and Newton[22] indicates the most likely outcome of the reaction of $C(^1S)$ in hydrocarbons to be either no reaction or dissociation with eventual deactivation to $C(^1D)$.

Interpretation of reaction products was greatly simplified by having to consider only two species, $C(^3P)$ and $C(^1D)$.

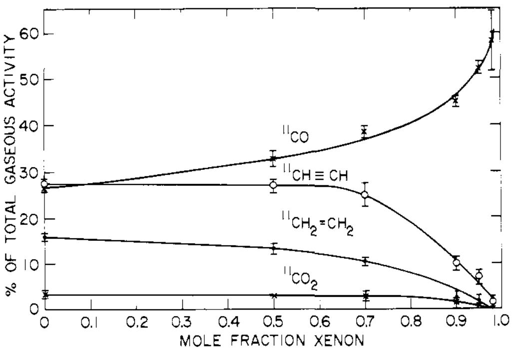

Figure 1. Absolute yields of major labeled products in ethane-oxygen-xenon mixtures. Errors represented are one standard deviation.

Arguments based on conservation of spin[16] led to the hypothesis that C(^{3}P) can insert into C–H bonds to give acetylene-^{11}C and other fragmentation products and that only the C(^{1}D) could insert into the C=C of unsaturated molecules to give substituted allenes-^{11}C.

While accepting the reasoning that C(^{3}P) can be responsible for acetylene-^{11}C production, Finn et al.[5] reported work which suggested a more subtle relationship for C(^{1}D) in saturated hydrocarbons. While these workers did not comment on the possible spin state of the ethylene-^{11}C precursor, they did suggest that the varying ratio of acetylene-^{11}C-ethylene-^{11}C with mole fraction of rare gas present indicated a higher energy mode of formation for acetylene-^{11}C than for ethylene-^{11}C. In addition, a small amount of acetylene-^{11}C was always observed in systems containing 99.5% rare gas, where thermalization of carbon atoms should be complete. Since all C(^{3}P) in this energy range should have been removed by oxygen scavenger, C(^{1}D) was indicated as the low-energy acetylene-^{11}C precursor. This assumption is consistent with experimental evidence obtained by Donovan and Husain,[22a] who found that low-energy C(^{1}D) can insert into C–H bonds in alkanes, giving acetylene.

Nicholas et al.[23] suggested the possibility of spin conversion in their study of moderator-ethylene systems, but essentially confined their attention to the role of energy in product distribution. Similarly, Peterson[24] conceded that relative amounts of C(^{3}P) and C(^{1}D) may change with moderation, but did not further explore this possibility.

Our experiments attempt to further assess the role of spin states on the reaction of carbon atoms by selectively removing C(^{1}D) and observing the effect on product yields. The use of xenon in our systems is based on the data of Husain and Kirsch,[25] whose spectroscopic measurements of the rate of disappearance of thermal C(^{1}D) in the presence of rare gases indicate an extreme sensitivity to xenon. One collision in three with xenon atoms was found to result in deactivation to the electronic ground state, compared to 1×10^6 collisions required in helium and 2×10^5 collisions in neon. This property of xenon makes it possible to deplete the supply of ^{1}D carbon which is available for reaction. Helium and neon provide "standard" behavior, where spin conversion is not expected to be important. These same rare gases have long been used by hot atom chemists to remove translational energy from reactants and thereby distinguish the products of hot and thermal reactions.[26] Reaction in helium and neon should occur before appreciable conversion of C(^{1}D) to the ground state.

The plot of ethylene-^{11}C yields vs. helium and neon gas concentration in Figure 2 shows generally the trends expected from the moderation of "hot" ^{11}C atoms by the rare gas molecules, resulting in an attenuation of the ethylene-^{11}C yields, neon being slightly more effective than helium. However the more pronounced drop of the ethylene-^{11}C yields in xenon is remarkable when compared with the much smaller effect seen in neon, although in the latter system energy transfer is expected to be approximately three times as efficient as in xenon. Thus, this phenomenon cannot be solely explained by energy moderation of the ^{11}C atom. Since C(^{1}D) is efficiently converted to C(^{3}P) in collisions with xenon it is reasonable to correlate the drastic reduction in the ethylene-^{11}C yields with the loss of C(^{1}D) due to conversion to C(^{3}P) and the failure of the energetic C(^{3}P) formed in the spin conversion to generate methyne-^{11}C, which subsequently could insert into the hydrocarbon to yield ethylene-^{11}C.[27] This is consistent with the theoretical calculations by Blint and Newton,[22] who postulate that energetic C(^{1}D) atoms could yield a temporary insertion complex (eq 1) which, however, could not be stabilized and decomposes to yield methyne in the $^2\pi$ state. This species could insert into a C–H bond, leading subsequently to ethylene formation (eq 4 and 5).[28]

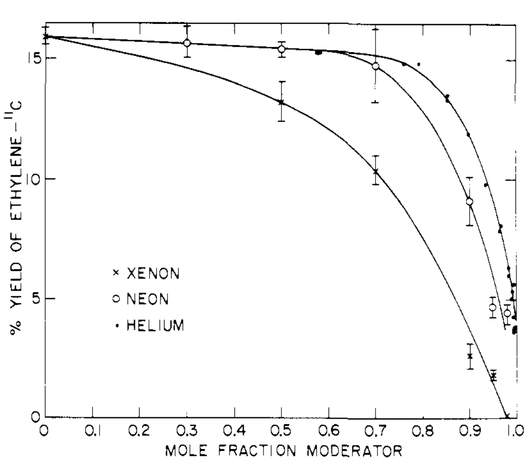

Figure 2. Variation of ethylene-^{11}C yield in ethane-oxygen-rare gas mixtures. Errors represented are one standard deviation. Each point in the helium curve represents a single determination.

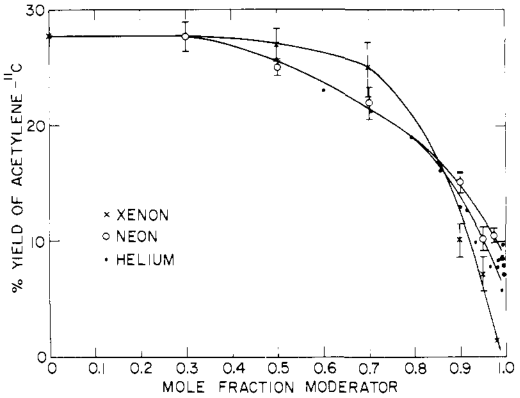

Figure 3. Variation of acetylene-^{11}C yield in ethane-oxygen-rare gas mixtures. Errors represented are one standard deviation. Each point in the helium curve represents a single determination.

The same authors[22] predict that energetic C(^{3}P) could yield a similar temporary insertion complex (eq 1) with a sufficient lifetime for internal energy transfer and bond breakage leading to acetylene.

Based on the latter prediction one might expect the yield of acetylene-^{11}C to rise with increasing amounts of xenon, due to the larger concentration of energetic C(^{3}P) from C(^{1}D) conversion. However, the simultaneous increase in energy degradation would also lead to reduction in acetylene-^{11}C yield due to loss of kinetic energy by the C(^{3}P) in collision with the noble gas and the consequent smaller number of ^{3}P carbons with energies above the threshold for the initial insertion reaction (eq 1).

The total acetylene-^{11}C yields will therefore be determined by two opposing factors. The results in Figure 3 where the

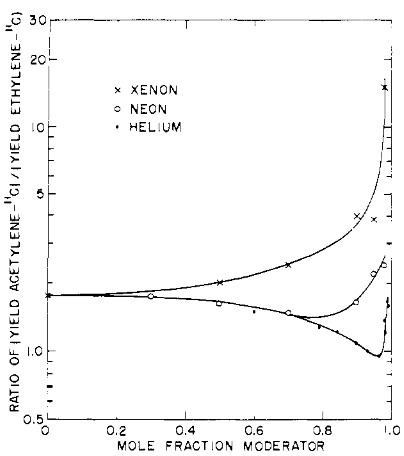

Figure 4. Variation of acetylene-^{11}C–ethylene-^{11}C ratio in ethane–oxygen–rare gas mixtures.

acetylene-^{11}C yields are plotted as a function of moderator concentrations show a decrease of acetylene-^{11}C in all three systems even in the case of xenon. Energy degradation is still the more dominating factor of the two and can compensate or overcompensate the opposing spin conversion effect.

At lower carbon energies stabilization of the ^{1}D insertion complex might be possible leading to acetylene-^{11}C formation, whereas reaction becomes impossible with C(^{3}P).[22] Thus this latter species is scavenged by oxygen. This may be an explanation for the crossing of the curves at 0.9 mole fraction noble gas. The xenon curve drops rapidly to zero, since C(^{3}P) is no longer sufficiently energetic to produce acetylene-^{11}C. The neon and helium curves never fall below about 5% acetylene-^{11}C, due to the relative abundance of low-energy ^{1}D carbon.

The variation of the ratio of acetylene-^{11}C–ethylene-^{11}C with mole fraction of these three different rare gases is plotted in Figure 4. In helium, where only energy moderation should be taking place, the ratio falls continually until 99% moderation is reached. Clearly, energy moderation is reducing the concentration of C(^{3}P) species, sufficiently energetic to form acetylene-^{11}C, faster than it is reducing the concentration of ethylene-^{11}C precursors. The situation in xenon is dramatically different, since the effect of energy degradation is smaller and is opposed by the rapid conversion of C(^{1}D) to C(^{3}P). Since the intermediate methyne-^{11}C cannot form, ethylene-^{11}C cannot be produced and the ratio rises rapidly. At very high helium and neon concentrations all carbon species are thermalized without much spin conversion having taken place. The presence of high concentrations of thermal C(^{1}D) promotes acetylene-^{11}C formation so that the ratio rises in this region. Neon represents an intermediate situation. Energy degradation is slightly more efficient in neon than in helium, so that the upward tendency materializes at lower concentrations.

Conclusions

The use of xenon as moderator and spin converter made it possible to identify specific electronic states of carbon atoms reacting with saturated hydrocarbons, allowing the assessment of the contributions made by these species to the formation of the various reaction products.

By combining the present experimental data with the results of previous investigation and published theoretical calculations, a clearer picture of these microscopic reactions emerges. At high energies C(^{3}P) primarily attacks C–H bonds to form acetylene-^{11}C and C(^{1}D) produces ethylene-^{11}C via insertion, followed by decomposition to ^{11}CH. At lower energies, C(^{1}D) may form acetylene-^{11}C, although the pathway to ethylene-^{11}C is no longer feasible. Thermalized C(^{3}P) in these systems is not reactive toward hydrocarbons and is effectively scavenged by oxygen. Although evidence suggests that acetylene-^{11}C is formed at higher energies than is ethylene-^{11}C, the precise energy ranges involved cannot be specified in the light of present information and should be the object of future investigations.

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References and Notes

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(27) The fact that Xe quenches C(^{1}D) one collision in three and that hydrocarbons are expected to reactively quench C(^{1}D) one collision in 10–50 suggests that the yield of ethylene at 50% moderation with Xe (Figure 2) should be considerably lower relative to the unmoderated yield if C(^{3}P) does not participate in this reaction. Not counting the kinetic energy degradation, since it is at best minor as shown by the He and Ne curves, one would expect a yield of something like 5% at half dilution unless the quenching rate at high energy is considerably poorer for Xe and better for C_2H_6 than reported. We are indebted to one of our referees for this comment.
(28) Both energetic C(^{3}P) and C(^{1}D) could yield CH directly by abstraction, but a significant portion of the CH arising from C(^{3}P) would be in the $^4\Sigma^-$ state, which would not insert into a C–H bond to yield ethylene.