substituent is the primary yield-determing factor.

Semiempirical calculations were used to estimate the intermediates in $^{76,77}\mathrm{Kr} \rightarrow {}^{76,77}\mathrm{Br}$ ipso substitution based on a two-step addition–elimination mechanism.[62] These calculations indicate that the second transition state involving bond breakage of the displaced substituent is the highest energy step, explaining the close relationship between the ipso substitution yield and bond energy. These calculations also indicate that free-radical displacement is much more favorable than nucleophilic substitution, showing agreement with the results of $^{76,77}\mathrm{Kr} \rightarrow {}^{76,77}\mathrm{Br}$ aromatic bromodeprotonation. Apparently, as in the latter case, reduction of reactive bromonium cations occurs until the nucleogenic species is charge-exchange neutralized to bromine radicals. Since electron-captive decay ^{76}Kr produces relatively more Br^{n+} charged species than β^+-decay ^{77}Kr, the ipso yield of ^{76}Br exceeds that of ^{77}Br.

Nucleophilic ipso substitution does not occur in monosubstituted benzene derivatives because the donated electron density from anionic bromdie leads to high-energy reaction intermediates. By adding substituents with electronegativity exceeding that of carbon, π-electron shielding of the ipso carbon atom nucleus is reduced, and stabilization of intermediate Meisenheimer adducts is achieved. Semiempirical calculations verified that the energy of all substitution intermediates can be decreased in this manner, and experimental verification was found by a biphasic linear free energy Hammett plot of nucleogenic aromatic bromodefluorination. For $^{76}\mathrm{Kr} \rightarrow {}^{76}\mathrm{Br}$, electron-donating substituents greatly increased the yield of radical ipso displacement of fluorine ($\rho \sim -0.7$), while electron-donating substituents also activated nucleophilic bromodefluorination ($\rho \sim +0.2$). By contrast, $^{77}\mathrm{Kr} \rightarrow {}^{77}\mathrm{Br}$ bromodefluorination showed a slower rate of enhancement of substitution yields with electron-donating substituents ($\rho \sim -0.4$), but a larger response to nucleophilic activation by electron-donating substituents ($\rho \sim +0.7$). These results are explanable on the basis of the charge spectra of the two bromine species resulting from the decay process of their krypton parents. ^{76}Kr decays via electron capture, generating primarily cationic species that are reduced to reactive bromine radicals, while ^{77}Kr decays chiefly by β^+ decay to generate a large fraction of nucleogenic ^{77}Br as reactive bromide anions.[21] This effect of substituent control over $^{76,77}\mathrm{Kr} \rightarrow {}^{76,77}\mathrm{Br}$ aromatic bromodefluorination gives credence to the two-step ipso addition–elimination mechanism and suggests that even greater yield effects are possible for larger halo substituents, where Meisenheimer complex formation rather than decomposition is the primary energy-demanding step.

Registry No. ^{76}Kr, 28522-17-0; ^{77}Kr, 14983-72-3; ^{76}Br, 15765-38-5; ^{77}Br, 15765-39-6; D, 7782-39-0; C_6H_6, 71-43-2; $C_6H_5CH_3$, 108-88-3; $C_6H_5C_2H_5$, 100-41-4; C_6H_5-i-C_3H_7, 98-82-8; C_6H_5-t-C_4H_9, 98-06-6; $C_6H_5NO_2$, 98-95-3; C_6H_5OH, 108-95-2; C_6H_5NH0, 62-53-3; $C_6H_5CF_3$, 98-08-8; $C_6H_5OCH_3$, 100-66-3; C_6H_5CN, 100-47-0; C_6H_5F, 462-06-6; C_6H_5Cl, 108-90-7; C_6H_5Br, 108-86-1; C_6H_5I, 591-50-4; p-$FC_6H_4NO_2$, 350-46-9; p-$FC_6H_4COCH_3$, 403-42-9; p-$FC_6H_4CF_3$, 402-44-8; p-FC_6H_4Br, 460-00-4; p-FC_6H_4I, 352-34-1; p-FC_6H_4F, 540-36-3; p-$FC_6H_4CH_3$, 352-32-9; p-$FC_6H_4OCH_3$, 459-60-9; p-FC_6H_4OH, 371-41-5; p-$FC_6H_4NH_0$, 371-40-4; o,p-$FC_6H_3(NO_2)_2$, 70-34-8; C_6F_6, 392-56-3; H, 1333-74-0.

Reaction Selectivity of Translationally and Electronically Excited Carbon-11 Atoms with Ethylene[1]

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Abstract: Measurement of the ^{11}C distribution in allene-^{11}C provided a means to distinguish the extent to which recoil carbon-11 atoms underwent C—H and C=C insertion pathways into ethylene. Combined moderator and scavenger studies also provided a means to alter the translational energy and electron spin distributions of the carbon-11 atoms. Results from these studies indicated that at the upper end of the energy range where carbon atoms become chemically reactive, C=C insertion occurred preferentially over C—H insertion for both $C(^3P)$ and $C(^1D)$ atoms. At the low end of the energy range, $C(^3P)$ carbon atoms reacted preferentially via C—H insertion. On the other hand, $C(^1D)$ atoms were not reactive toward C—H insertion, at least in the formation of allene-^{11}C.

The present model of carbon atom chemistry has evolved largely through two decades of effort where elaborate techniques to generate and to study the atom–molecule chemistry include nuclear recoil,[2-5] thermal evaporation,[6] thermal decomposition,[7] and photolytic decomposition[8] methods. The quadravalent carbon atom was predicted to undergo a set of characteristic reactions in order to reduce its electron deficiency. According to the present model, carbon atom reactions with hydrocarbons were categorized as (i) insertion into C–H bonds,[9,10] (ii) addition to carbon–carbon double bonds,[11-13] and (iii) abstraction of hydrogen from hydrocarbons.[14-20]

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While there seems to be an abundance of published work dealing with recoil carbon-11 atom chemistry and the qualitative correlation of observed products to the reaction model for carbon atoms, as it is presently understood, less effort has been made to assess the effects of excess translational and electronic excitation of the recoil carbon-11 atom on its subsequent chemistry. Part of the problem is due to the fact that the recoil atom generally carries a large excess of translational energy into the reaction coordinate. This results in secondary processes such as dissociation and bimolecular reaction which generally shadow primary reaction events of the atom. Also, the carbon atom is known to exist in three low-lying electronic states. It possesses a ^3P ground state with zero energy, and ^1D and ^1S excited states with 1.7 and 2.3 eV energies, respectively. Recoil carbon atoms are produced and react to some extent in all three electronic states, yet very little is known regarding the $^3P/^1D/^1S$ ratio produced in the nuclear recoil system or what effect the electronic state has on the reaction modes of the recoil carbon atom.

Specific studies, utilizing the radiolytic dissociation of carbon suboxide as the atomic carbon source, have been performed to distinguish the reactivity of $C(^3P)$ and $C(^1D)$ atoms with specific hydrocarbons.[21-24] These studies, however, dealt with very low translational excitation of the atom due to the energy limitations of the generation methods employed. Ab initio calculations by Newton also have given insight into correlations of atomic carbon chemical reactivity and reaction selectivity with translational and electronic excitation of the atom for a simple H_2 model.[25] Results from these calculations indicated that collision of $C(^1S)$ atoms with a substrate would lead to either no reaction or dissociation. This suggested that only $C(^3P)$ and $C(^1D)$ atoms were responsible for stable product formation in the reaction coordinate. Extensive quasiclassical trajectory calculations by Kroger et al. using a valence bond diatomics-in-molecules potential energy surface have also given insight into translational excitation effects (in the 0.1–10 eV range) on the X-abstraction mechanism by $C(^1D)$ atoms in a simple HI model.[26] Experimental studies by Taylor et al. have suggested that observed perturbations in the "hot" fragmentation chemistry following C–H insertion by recoil carbon-11 atoms, in systems employing xenon as an efficient ^1D-to-^3P spin convertor of the atom, could be evidence for differing chemistry of the atomic carbon on the basis of its electronic excitation.[27]

The present investigation focussed on the effects of translational and electronic excitation on carbon-11 atom reactivity with regard to C—H and C=C insertion pathways. Reaction of a carbon atom with ethylene by either of these two pathways would produce allene-*1*-^{11}C or allene-*2*-^{11}C, respectively. A chemical means was employed to distinguish the yields of these two products. This served as a measure of the extent to which each pathway occurred.

Experimental Section

Materials. The ethylene used in all experiments was research grade (Matheson, >99.97% purity) and was further purified of trace oxygen by conventional degassing techniques on a vacuum line. Neon (Matheson, research grade, >99.998% purity) and oxygen (Matheson, research grade, >99.98% purity) were used without further purification. Potassium permanganate used in the oxidative degradation method was obtained from the Aldrich Chemical Co.

Sample Preparation. Neat ethylene samples were prepared for irradiation by sealing between 200 and 1600 torr of the gas into a 30-cm^3 quartz irradiation vessel equipped with a Teflon-brand stopcock. For mixed ethylene–neon, ethylene–oxygen, or ethylene–oxygen–neon samples, a 250-cm^3 aluminum vessel was employed equipped with a Hoke stainless steel shot-off valve. The procedure required first filling the vessel with 200 torr of ethylene; the vessel was then reequilibrated with higher pressures of oxygen and/or neon gas.

Irradiations. The irradiations were carried out using a 33-MeV proton beam from the Brookhaven 60-in. Cyclotron, where recoil carbon-11 atoms were generated via the $^{12}C(p,pn)^{11}C$ nuclear transformation. The (p,pn) reaction was chosen because its use minimized radiolytic consequences in the beam strike area. All irradiations of gases were carried out at the ambient temperature of the cyclotron vault (~25 °C). The proton beam entered the reaction vessels either through a 10×10^{-3} in. quartz or aluminum window depending on which target vessel was employed. Typical beam intensities were 1 μA with exposure times of 100 s. Radiation doses were 3.5×10^{-4} eV molecule^{-1} μA^{-1} s^{-1} as determined by acetylene to benzene dosimetry.[28] In the neon and oxygen additive studies, the radiation dose was varied 20-fold to ascertain that observed changes in the product distribution were not due to radiation-sensitized processes.

Radioassay of ^{11}C Activity and Allene-^{11}C Purification. Following irradiation, the total volatile carbon-11 activity (TVA) was determined by counting a 1-mL aliquot of the gas sample using a well-type NaI (Tl) scintillation crystal. This was accomplished by withdrawing the aliquot directly from a septum on the vessel using a Teflon-brand sealed gas syringe (Precision Sampling Corp.). The aliquot was injected into a preevacuated 10-mL tube that was also equipped with a septum. The remainder of the sample was cryogenically transferred into a loop for injection into a radio gas chromatograph. The radioactive compounds eluting the column were measured in the usual manner by using gas effluent counting.[29] Compound identification was made on the basis of its retention index relative to authetic samples on three columns: (i) a 25-ft column of 10% dimethylsulfolane (DMS) packed on 80–100 mesh Chromosorb P; (ii) a 12-ft Porapak Q column of 80–100 mesh; and (iii) a 25-ft column of 10% squalane packed on 80–100 mesh Chromosorb P.

The nonvolatile products deposited on the inside of the irradiation vessel surface were measured by washing the vessel with propanone and methanol and counting aliquots of these washings. The total carbon-11 activity (TA) was determined by summing the combined volatile and nonvolatile activities after appropriate radioactive decay and fraction corrections were made. The individual volatile product yields were calculated by dividing the decay-corrected integrated peak activities from the effluent counter by the TA.

Allene-^{11}C was purified through preparative gas chromatography using a 6-ft silver nitrate column in series with the 25-ft DMS column. The silver nitrate column mainly served to remove the large yield of acetylene-^{11}C generated in this recoil system. The 25-ft DMS column then achieved satisfactory separation of allene-^{11}C from the remainder of the complex carbon-11 product spectrum.

Degradation of Allene-^{11}C. In the first step of the degradation procedure, allene-^{11}C was hydrolyzed to propanone-^{11}C, reaction 1. The

$$H_2C{=}C{=}CH_2 \xrightarrow[Ag_2SO_4]{aq\ H_2SO_4} H_2C{=}C(OH)CH_3 \rightarrow H_3CC({=}O)CH_3 \quad (1)$$

hydrolysis was effected by introducing the purified allene-^{11}C (mixed with carrier allene) into a helium flow stream (16 mL/min) that passed through a silica gel column impregnated with water, sulfuric acid, and silver sulfate and maintained at 194 °C.[30] The hydrolysis packing was prepared by mixing 50 g of 28–200 mesh silica gel with 5 g of silver sulfate, 29 mL of water, and 30 mL and 17 N sulfuric acid. This mixture was baked in an oven at 110 °C for approximately 30 h prior to use. The hydrolysis tube through which the gas stream flowed consisted of 12 × 0.25 in. o.d. Pyrex tube, the center 8 in. of which was packed with the treated silica gel. Propanone-^{11}C was separated from unreacted allene-^{11}C and any acid hydrolysates by flowing the gas effluent through a series of three U-traps: the first was maintained at 0 °C with an ice bath and removed hydrolysates from the flow stream; the second was maintained at −104 °C with a cyclohexane–liquid nitrogen slurry and removed propanone-^{11}C; the third was maintained at −196 °C with liquid nitrogen and removed unreacted allene-^{11}C. Aliquots from both the propanone-^{11}C and allene-^{11}C traps were then analyzed to determine the percent conversion. Generally between 50% and 75% of the allene-^{11}C was converted

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Table I. ^{11}C-Product Distribution from Carbon-11 Atom Reactions with Ethylene[a]

product	yield, % TA
CO	0.6 ± 0.1
CH_4	<0.05
CO_2	
C_2H_6	<0.1
C_2H_4	0.6 ± 0.1
C_2H_2	19.3 ± 1.5
C_3H_8	<0.05
propylene	1.4 ± 0.3
cyclopropane	1.6 ± 0.3
allene	8.5 ± 1.0
propyne	2.3 ± 0.2
$C_4 + C_5$	13.3 ± 1.6
higher boiling volatiles[b]	28.5
nonvolatile products[c]	23.7

[a] The product distribution was measured at 200 torr ethylene pressure. [b] The high-boiling volatile products were measured as TVA−$\Sigma C_1 + C_2 + ... + C_5$. [c] The nonvolatile product yield was measured from the vessel wall washings and bulk counting of liquid aliquots on the γ-well counter.

to propanone-${}^{11}C$ under these reaction conditions.

The solvent-free heterogeneous oxidation of propanone by hot potassium permanganate in a flow stream yielded carbon dioxide as the final oxidized product from the center carbon and a mixture of formaldehyde and formic acid from the terminal carbons. Studies using propanone-${}^{14}C$ in the form of $(CH_3)_2{}^{14}CO$ and $({}^{14}CH_3)_2CO$ established that these products were the result of a stepwise oxidation mechanism.[31] In the first stage of oxidation, propanone was degraded to formaldehyde and acetic acid. However, subsequent oxidation of these primary products produced formic acid from formaldehyde and formaldehyde plus carbon dioxide from acetic acid where the carbon dioxide was produced from the carboxyl carbon. The degree of oxidation was observed to be temperature dependent. However, optimized oxidation conditions were attained (when 100% oxidation of acetic acid occurred) at a reaction temperature of 240 °C. Care must be taken since at higher temperatures both formaldehyde and formic acid will be oxidized to carbon dioxide.[31]

In the actual degradation of propanone-${}^{11}C$, the labeled compound, mixed with carrier propanone, was flowed through a 12 × 0.25 in. Pyrex tube packed with 5 g of potassium permanganate maintained at 240 °C. A helium sweep gas was employed where the flow rate was regulated to about 20 mL/min. The oxidized products were either removed from the sweep gas through standard cryogenic trapping procedures and later analyzed by radio gas chromatography or flowed directly into the radio gas chromatograph for on-line analysis.

^{11}C-Labeled Product Analysis from Allene-${}^{11}C$ Degradation. Analyses of the ^{11}C-labeled products from the oxidative degradation of allene-${}^{11}C$ were carried out using a radio gas chromatograph equipped with a thermal conductivity response detector and a Wolf flow-through gas proportional counter.[32] Product separation was effected by passing the compounds through as 10 ft. × 0.25 in. o.d. column packed with 80–100 mesh Porapak Q-S and maintained at 145 °C. Oxidation products were identified by comparing retention times of the activity peaks with those of authentic compounds. Also, in unlabeled experiments a comparison was made between the infrared spectra of authentic samples and the individual products.

A major modification to the standard ratio gas chromatograph was the inclusion of an effluent combustion chamber at the column outlet.[33,34] The combustion chamber, made of 0.2-in. i.d. quartz tubing and filled with oxidized copper wool, was operated at about 800 °C. Here the carbon-11 labeled compounds were quantitatively oxidized to carbon dioxide-${}^{11}C$ and water. Water was removed by means of a magnesium perchlorate trap located at the exit port of the combustion tube. The carbon dioxide-${}^{11}C$ activity was measured in the flow-through gas proportional counter.

Results and Discussion

The ^{11}C-product distribution from carbon-11 atom reactions with ethylene at 200 torr were presented in Table I. All yields were reported as a percentage of the total ^{11}C activity (TA). The allene-${}^{11}C$ yield was measured at 8.5% TA. The overall product spectrum was complex yielding numerous C_4, C_5, and higher molecular weight products. Radicals formed via fragmentation and spin-disposal modes underwent efficient addition to ethylene resulting in such products. Contributions to the product spectrum from species such as ${}^{11}CH$, ${}^{11}CH_2$, or ${}^{11}CH_3$ were small as measured by the low yields of the more saturated products.

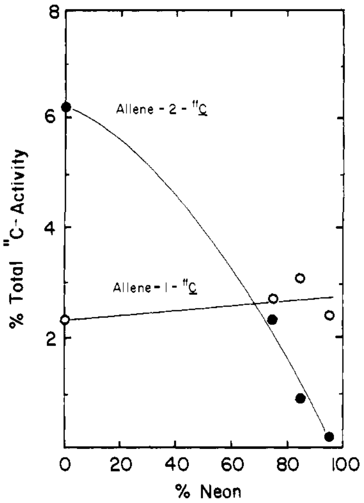

Figure 1. Effect of neon moderator on the yields of allene-*1*-${}^{11}C$ (○) and allene-*2*-${}^{11}C$ (●) for samples containing 200 torr of ethylene and increasing amounts of neon.

Formation of Allene-*1*-${}^{11}C$ and Allene-*2*-${}^{11}C$ from Recoil Carbon-11 Atom Reactions with Ethylene. Marshall et al. previously demonstrated that allene-*1*-${}^{11}C$ and allene-*2*-${}^{11}C$ could be produced through recoil carbon-11 atom interaction with the C=C or C—H bonds of ethylene, respectively, and observed 66% of this product to be center labeled.[13] The large yield of allene-*2*-${}^{11}C$ was attributed to efficient addition of the carbon-11 atom to the π-bond of ethylene, as seen in reaction 2, The 34% distribution of

$$ {}^{11}\underset{\cdot}{\text{C}}{:}^{*} + H_2C{=}CH_2 \rightarrow \underbrace{{}^{11}\ddot{C}CH_2CH_2} \rightarrow H_2C{=}{}^{11}C{=}CH_2 \quad (2) $$

allene-*1*-${}^{11}C$ observed in this study was attributed to C–H insertion by the carbon-11 atom, as seen in reaction 3, followed by a hydrogen shift.

$$ {}^{11}\underset{\cdot}{\text{C}}{:}^{*} + H_2C{=}CH_2 \rightarrow H^{11}\underset{\cdot}{\dot{C}}{-}CH{=}CH_2 \rightarrow H_2{}^{11}C{=}C{=}CH_2 \quad (3) $$

In the present work we have confirmed the experimental result of Marshall et al. using similar preparative and experimental conditions but a different degradation method.[31,35] In four neat ethylene samples, the average yield of allene-*2*-${}^{11}C$ was 6.2% TA per sample while the average yield of allene-*1*-${}^{11}C$ was 2.3% TA. This transcribed into an average of 73.8 ± 4.3% distribution for the center-labeled allene-*2*-${}^{11}C$. This value was independent of pressure with between 200 and 1600 torr of ethylene.

Effect of Neon Moderator on the ^{11}C Distribution in Allene-${}^{11}C$. The addition of neon to the gas system has the effect of increasing the number of nonreactive collisions that the carbon-11 atom undergoes prior to a reactive collision with the substrate. These collisions result in the transfer of translational energy between the atom and moderator. Therefore, an increase in the neon concentration would lower overall energy distribution of the carbon atoms.[36] Reaction channels open to the carbon atoms in the high-energy region can become less significant as other channels effectively compete at the lower energies.

Presented in Figure 1 are the absolute yields measured for allene-*2*-${}^{11}C$ and allene-*1*-${}^{11}C$ as a function of the molar concen-

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tration of neon moderator. As the neon concentration was increased to 95 mol % the allene-*2*-^{11}C yield decreased from 6.2% to less than 0.2% TA, while the allene-*1*-^{11}C yield increased only slightly from 2.3% to 2.7% TA. The observed sharp decrease in the allene-*2*-^{11}C yield with increasing neon concentration indicated that the carbon atoms in the pure system that produced allene-*2*-^{11}C were highly energetic. This result was consistent with the observation that the total allene-^{11}C yield decreased by 70% of its original gas-phase yield as increasing amounts of neon were added to the system.[15] This fact in itself suggested that the major reaction channel for allene-^{11}C formation from ethylene must be a high-energy process. On the other hand, the slight increase in the allene-*1*-^{11}C yield indicated that the carbon atoms yielding this product via a C–H insertion pathway were somewhat more thermal.

As pointed out earlier, Marshell et al. suggested that the double-bond interaction in the allene-*2*-^{11}C pathway occurred via π-addition of the carbon atom (reaction 1) to produce a cyclopropylidene intermediate.[13] In view of the high-energy dependence observed in the present work for this double-bond interaction mechanism, a concerted insertion mechanism could also be a viable path to allene-*2*-^{11}C. Final product analysis did not alloy a distinction to be drawn between these two processes.

Effect of Oxygen Scavenger on the Electronic Spin Distribution of the Carbon-11 Atoms. The study of the electronic spin distribution of carbon-11 as a function of oxygen is informative in that it allows one to focus on the singlet carbon atom reactions with ethylene. The ability of oxygen to scavenge triplet species is 2-fold in the systems under study here. The major portion of the scavenging effect is observed in the removal of $C(^3P)$ atoms. Secondary effects are due to the removal of free-radical reaction intermediates. These results were evident where carbon atoms were generated either photolytically or by microwave discharge from the decomposition of carbon suboxide and allowed to react with oxygen, methane, and ethylene.[22-24,37] It was apparent from these studies that thermal $C(^3P)$ atoms were 10^5 times more reactive toward oxygen scavenging than towards C–H insertion or π-bond interactions in hydrocarbons. Indeed, the reaction of thermal $C(^3P)$ with oxygen occurs on nearly every collision. On the other hand, the relative rate constant ratio between oxygen scavenging and C–H insertion into methane by thermal $C(^1D)$ atoms was measured at 0.125[37] and 0.156.[23] The same ratio was measured at 0.07[37] and 0.014[23] between oxygen scavenging and reaction with ethylene. Therefore, it seems likely that increasing oxygen concentrations should diminish the thermal $C(^3P)$ population in the reaction coordinate. However, very little can be said from these results about the reactivity of translationally hot $C(^3P)$ atoms in the ethylene system.

In order to ascertain the scavenging ability of oxygen in the recoil carbon-11 ethylene system where reaction energies were considerably higher, the total allene-^{11}C yield was monitored as a function of oxygen concentration. Also, the oxidation products, carbon-^{11}C monoxide and carbon-^{11}C dioxide, were monitored in the same study. Results in Figure 2 illustrate the absolute yields observed for allene-^{11}C, carbon-^{11}C monoxide, and carbon-^{11}C dioxide as a function of the oxgyen molar concentration. Results indicated a drastic increase in the carbon-^{11}C monoxide yield to a plateau of 32% TA with slightly greater than 20 mol % of oxygen scavenger. A small yield of carbon-^{11}C dioxide was also detected, ~5% TA, where its formation was attributed to radiolytic oxidation of carbon-^{11}C monoxide or other organic species in the gas.[38]

Over the same oxygen concentration range the total allene-^{11}C yield decreased from 8.5% and leveled at 4.7% TA. The decrease in the allene-^{11}C yield was more than compensated by the increase in the combined ^{11}C-labeled oxide yield. However, allene-^{11}C was only one of several hydrocarbon products in the ethylene system that decreased in yield due to oxygen scavenging. Table II presents an overview of the change in the ^{11}C-product distribution as a function of oxygen scavenging. Results indicated that the ~40% TA increase in the combined ^{11}C-labeled oxide yield was compensated by an ~30% TA decrease in the ^{11}C-labeled volatile hydrocarbon phase, and an ~10% TA decrease in the ^{11}C-labeled nonvolatile phase. Since very little change in the combined oxide yield was observed between 20 and 60 mol % oxygen, it seemed apparent that the scavenging effect was optimized in this range. This suggested that about 60% of the carbon atoms escaped scavenging through more accessible reaction channels with ethylene either because of their spin state ($C(^1D)$ atoms) or because of their excess translational energy (hot $C(^3P)$ atoms). To test the later premise, neon was added to oxygen-scavenged ethylene samples (approximately 3:1 ethylene/oxygen) in order to thermalize the hot $C(^3P)$ atoms. Contributions to the $C(^3P)$ population due to collisional quenching of $C(^1D)$ by neon should not be significant since the rate constant ratio of collisional quenching by neon to $C(^1D)$ reaction with ethylene is about 10^{-6}.[24,37] In light of this, the increase in the carbon-^{11}C monoxide yield from 32% to 56% TA with up to 88 mol % neon (illustrated in Figure 3) could be attributed to the increased population of thermal $C(^3P)$ atoms from thermalization of hot $C(^3P)$ atoms by neon. However, this view rests on the assumption that the neon quenching efficiency is low. It must be noted that a high quenching efficiency would also increase the $C(^3P)$ population and produce the same experimental results.

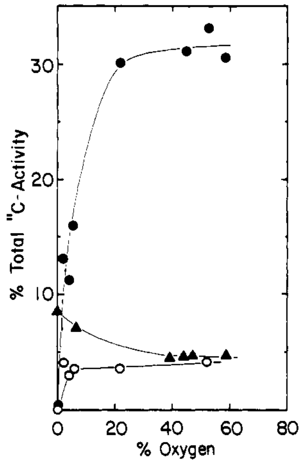

Figure 2. Effect of oxygen scavenger on the yields of carbon-11 labeled allene (▲), carbon monoxide (●), and carbon dioxide (○) for samples containing 200 torr of ethylene and increasing amounts of oxygen.

Table II. Effect of Scavenger on the ^{11}C-Product Distribution (% TA) in the Ethylene System[a]

% oxygen	$^{11}CO + {}^{11}CO_2$	volatile hydrocarbons $C_2 + C_3$	higher boiling[b]	nonvolatile product[c]
0	0.6	33.9	41.8	23.7
9	19.6	23.6	35.2	21.6
40	37.9	19.7	21.3	21.1
52	41.6	15.0	30.4	13.0
65	41.9	14.3	30.7	13.1

[a] Sample substrate pressures were maintained at 200 torr ethylene, with increasing amounts of oxygen scavenger added in. [b] The higher boiling volatile products were measured as TVA − $(C_1 + C_2 + C_3)$. [c] The nonvolatile product yield was measured from the vessel wall washing and bulk counting of liquid aliquots on the γ-well counter.

Effect of Oxygen Scavenger on the ^{11}C Distribution in Allene-^{11}C. The distribution of carbon-11 in allene-^{11}C was monitored as a function of oxygen concentration in order to gain some insight into the reaction selectivity of carbon atoms between C—H and C=C bonds relative to their electronic excitation. Presented in Figure 4 are the absolute yields measured for allene-*2*-^{11}C and allene-*1*-^{11}C as a function of the molar concentration of oxygen scavenger. Results indicated that as the oxygen concentration was increased to 45 mol %, the allene-*2*-^{11}C yield decreased and leveled off at 4.7% TA, while the allene-*1*-^{11}C yield *was completely*

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(37) Husain, D.; Kirsch, L. J. *Trans. Faraday Soc.* **1971**, *67*, 2025.
(38) Ache, H. J.; Wolf, A. P. *J. Phys. Chem.* **1968**, *72*, 1988.

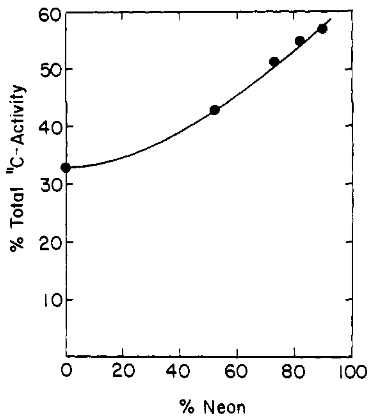

Figure 3. Effect of neon moderator on the carbon-^{11}C monoxide yield for samples containing 200 torr of ethylene/oxygen (3:1) and increasing amounts of neon.

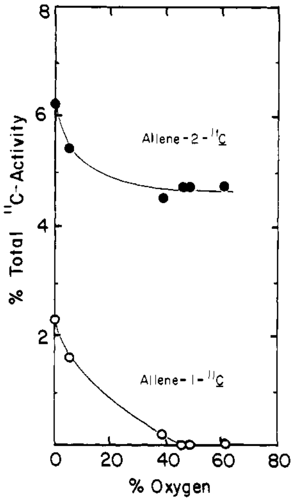

Figure 4. Effect of oxygen scavenger on the yields of allene-*1*-^{11}C (○) and allene-*2*-^{11}C (●) for samples containing 200 torr of ethylene and increasing amounts of oxygen.

eliminated. That is to say, that at 45 mol % oxygen the ^{11}C distribution in allene-^{11}C was found to be 100% center labeled.

In light of the previous discussion on the spin distribution effects of oxygen in the recoil carbon-11 ethylene system, the decreased yields of both allene-*2*-^{11}C and allene-*1*-^{11}C with oxygen indicated that $C(^3P)$ atoms were precursors to both products. Also, the fact that the allene-*1*-^{11}C yield was completely eliminated suggested that $C(^1D)$ atoms (both energetic and thermal) were apparently selective in undergoing exclusive C=C insertion to yield allene-*2*-^{11}C.

Energy Considerations on $C(^1D)$ Selectivity. The nonreactive nature of $C(^1D)$ atoms in producing stable allene from a C–H insertion mechanism was tested in a final study designed to distinguish the selectivity of translationally hot and thermal $C(^1D)$ atoms undergoing reaction with ethylene. For this study, the ^{11}C distribution in allene-^{11}C was monitored as a function of neon moderator in oxygen scavenged ethylene samples (3:2 ratio of ethylene/oxygen). As seen in Figure 5, up to 85 mol % of neon resulted in a drastic decrease in the allene-*2*-^{11}C yield from 4.7% to 0.14% TA with only a slight increase in the allene-*1*-^{11}C yield from 0% to 0.27% TA.

Given the assumption that the quenching efficiency of neon was low, samples containing a concentration of neon moderator would reflect the chemistry of only thermal $^{11}C(^1D)$ atoms. The above results would imply that even thermal $^{11}C(^1D)$ was not reactive toward C–H insertion to yield allene-*1*-^{11}C. Even if the neon quenching efficiency was substantial enough to increase the $^{11}C(^3P)$ population, then in the presence of oxygen, the $^{11}C(^3P)$ atoms would have been more effectively scavenged as ^{11}CO and not reacted with ethylene. This might explain the 91% decrease in the total allene-^{11}C yield observed in the present system with subsequent increases in the ^{11}CO yield (see Figure 3).

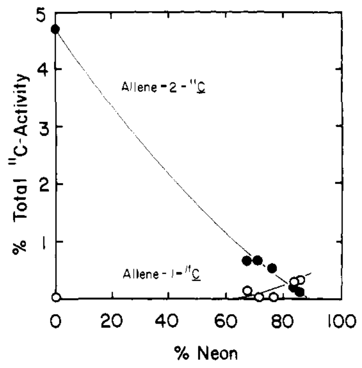

Figure 5. Effect of neon moderator on the yields of allene-*1*-^{11}C (○) and allene-*2*-^{11}C (●) for samples containing 200 torr of ethylene/oxygen (3:2) and increasing amounts of neon.

In view of these results, two considerations should be pointed out. First, those thermal $C(^1D)$ atoms that may have undergone C–H insertion to produce allene-*1*-^{11}C in the "pure" ethylene system may have produced radical intermediates that were susceptibile to oxygen scavenging in the present studies. This was not likely, however, for two reasons. First, volatile ^{11}C-labeled oxygenated organic species were not detected in the product spectrum. Furthermore, the results in Table II indicated that the increase in the combined ^{11}C-labeled oxide yield was substantiated by the falloff in the ^{11}C-labeled hydrocarbon yields. This indicated that primary scavenging of the atomic species and not of radical intermediates was the predominant effect.

A second consideration in the apparent selectivity of $C(^1D)$ for C=C insertion is that insertion of energetic $C(^1D)$ atoms into the ethylene C—H bond may have resulted in an adduct that underwent rapid decomposition. Studies by Taylor et al., in the atomic carbon reactions with alkanes, ascribe ^{11}CH production to C—H insertion by translationally excited $^{11}C(^1D)$ atoms into the alkyl substrate followed by decomposition of the resultant adduct.[14,27,39]

$$^{11}\underset{\cdot\cdot}{\mathrm{C}}(^1D) + \mathrm{H{-}CH_2R}\ (\mathrm{R} = n\text{-alkyl}) \rightarrow \mathrm{H}^{11}\ddot{\mathrm{C}}\mathrm{{-}CH_2R} \rightarrow :^{11}\dot{\mathrm{C}}\mathrm{H} + \mathrm{CH_2R} \quad (4)$$

Such a process may account for the fate of those $C(^1D)$ atoms in the present system that underwent C—H insertion. However, it was pointed out earlier that the yields of hydrocarbon products attributable to ^{11}CH and $^{11}CH_2$ chemistry were low in the present system.

Additional supportive evidence for the selectivity of $C(^1D)$ atoms toward C=C insertion may also be found in the work performed by Mullen and Wolf where carbon-*2*-^{14}C suboxide was photodissociated in the presence of ethylene to study the reactions of $^{14}C(^1D)$.[40] The positional ^{14}C distribution in the resultant allene-^{14}C product was found to be 92% center labeled. However, questions were raised whether $C(^1D)$ or C_2O was the reactive species in the system.

Spin Conservation Considerations in Selectivity Evaluation. In evaluating the reaction selectivity of $C(^1D)$ atoms with ethylene on the basis of spin conservation, there would be no spin restrictions on the rearrangement of the singlet C_3H_4 adduct formed following C-H insertion by these atoms. Therefore, formation of allene-*1*-^{11}C via $^{11}C(^1D)$ insertion into the C-H bond would be a spin allowed process.

$$\mathrm{C}(^1D) + \mathrm{H_2C{=}CH_2} \xrightarrow[\text{insertion}]{\text{C—H}} \mathrm{C_3H_4}\ (\text{singlet}) \rightarrow \mathrm{H_2{}^{11}C{=}C{=}CH_2} \quad (5)$$

The fact that no allene-*1*-^{11}C was detected from energetic or

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[39] Taylor, K. K.; Ache, H. J.; Wolf, A. P. *J. Phys. Chem.* **1978**, *82*, 2385.

[40] Mullen, R. T.; Wolf, A. P. *J. Am. Chem. Soc.* **1962**, *84*, 3214.

thermal $^{11}C(^1D)$ atoms undergoing C—H insertion indicates that this reaction does not occur.

$$C(^1D) + H_2C{=}CH_2 \xrightarrow[\text{insertion}]{\text{C—H}} \text{No reaction to yield allene-}\mathit{1}\text{-}^{11}C \quad (6)$$

While the selectivity of energetic $C(^1D)$ atoms for the C=C insertion over C—H insertion can be justified on the grounds of energetics, the apparent nonreactivity of thermal $C(^1D)$ atoms toward the ethylene C—H bonds may be due to more efficient thermal π-bond addition processes resulting in subsequent bimolecular reactions and polymerization.

$$^{11}C(^1D)\ (\text{energetic}) + H_2C{=}CH_2 \xrightarrow[\text{insertion}]{\text{C=C}} H_2C{=}^{11}C{=}CH_2 \quad (7)$$

$$^{11}C(^1D)\ (\text{thermal}) + H_2C{=}CH_2 \xrightarrow{\pi\text{-addition}} C_5 \text{ compounds and polymer} \quad (8)$$

Past gas-phase studies in the recoil carbon-11 ethylene system have shown increased C_5 product yields with increased neon moderation.[15] Evidence for the selective π-bond addition of thermal $^{11}C(^1D)$ atoms to 1,3-butadiene resulting in cyclopentadiene-^{11}C was also presented in a recent paper.[41]

Evaluation of the reaction selectivity of $C(^3P)$ atoms with ethylene on the basis of spin conservation becomes somewhat more complex. The insertion of energetic $^{11}C(^3P)$ atoms into the ethylene C=C bond to produce allene-*2*-^{11}C directly avoids the spin conservation rule since the initial reaction event results in bond rupture.

$$^{11}C(^3P)\ (\text{energetic}) + H_2C{=}CH_2 \xrightarrow[\text{insertion}]{\text{C=C}} H_2C{=}^{11}C{=}CH_2 \quad (9)$$

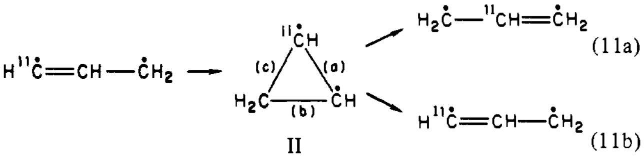
On the other hand, insertion of thermal $^{11}C(^3P)$ atoms into an ethylene C—H bond resulting in allene-*1*-^{11}C would be a spin-forbidden process if a simple rearrangement of hydrogen were to occur in the triplet adduct I.

$$^{11}C(^3P) + H_2C{=}CH_2 \xrightarrow[\text{insertion}]{\text{C—H}}$$

$$\left[H^{11}\underset{\bullet}{\dot{C}}{-}CH{=}CH_2 \underset{\text{I}}{\longleftrightarrow} H^{11}\dot{C}{=}CH{-}\dot{C}H_2\right] \xrightarrow{\text{H transfer}} \quad (10a)$$

$$H_2{}^{11}\dot{C}{-}\dot{C}{=}CH_2\ (\text{triplet}) \xrightarrow{\text{spin inversion}} H_2{}^{11}C{=}C{=}CH_2 \quad (10b)$$

However, the spin considerations could be circumvented by a plausible route where rearrangements of the triplet adduct I could proceed through a cyclization process.



II

(11a)

(11b)

In fact, thermolytically and photolytically generated vinylcarbenes have never been observed to yield allenic products from hydrogen shifts, but they undergo rapid intramolecular addition to yield cyclopropenes.[42] The cyclic intermediate II shown in reaction 11 should collapse through rupture of bonds b or c to produce center- and end-labeled forms of adduct I, but with mixed spin distributions due to the bond rupture. It is unlikely that the ring would remain intact because of the excess energy in the "intermediate". While cyclopropene was not directly sought in the present study, there were no unidentified products that could be attributed to it in the C_1–C_5 product spectrum. Marshall had considered intramolecular cyclization as a possible source of allene-*2*-^{11}C.[15] These authors suggested that a somewhat equal distribution of center- and end-labeled forms of adduct I, from collapse of the cyclic intermediate II, should be expected since rupture of bond a would require much more energy. In fact, results from the effects of oxygen scavenger on the ^{11}C distribution in allene-^{11}C in the present work showed a decrease in the allene-*2*-^{11}C from 6.2% to 4.7% TA corresponding to 1.5% TA, and a decrease in the allene-*1*-^{11}C yield from 2.3% to 0% TA. These results indicated that $C(^3P)$ atoms were producing *both* center- and end-labeled forms of allene-^{11}C in a distribution of 40% and 60%, respectively. This indicated that there was an equal probability for any single bond to rupture in the ring.

Conclusions

Two key observations were made in the present studies. The translational energy of the carbon atoms and their electronic spin states both affect the distribution of carbon-11 in allene-^{11}C. At the upper end of the energy range where carbon atoms became chemically reactive, C=C insertion was a dominant reaction pathway available to both spin states. This pathway may, however, be one of two sources for allene-*2*-^{11}C formation. At the lower end of the energy range, ^3P carbon atoms reacted with ethylene preferentially via C—H insertion. This pathway could lead to either allene-*1*-^{11}C or allene-*2*-^{11}C through intramolecular cyclization of the triplet adduct. On the other hand, ^1D carbon atoms were nonreactive toward C—H insertion in this low-energy range, at least in the allene-^{11}C product formation pathway.

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Registry No. Carbon-11, 14333-33-6; ethylene, 74-85-1.

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