Evidence for the Selective Addition of Thermal $^{11}C(^1D)$ Atoms to Carbon–Carbon Double Bonds

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The generation of [^{11}C]cyclopentadiene through the reaction of recoil carbon-11 atoms with buta-1,3-diene occurs by the selective addition of thermal $^{11}C(^1D)$ atoms to the carbon–carbon double bonds of the diene.
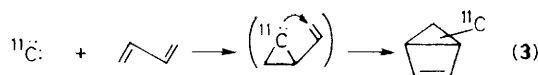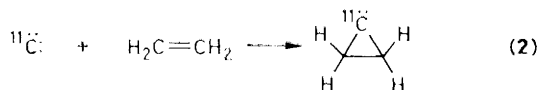
In a recent study, it was established that translationally excited $^{11}C(^1D)$ atoms were selective in undergoing direct double bond insertion into ethylene to yield [2-^{11}C]allene as shown in reaction (1), but that the corresponding reaction with thermalized $^{11}C(^1D)$ atoms did not proceed.[1] However, it was impossible to ascertain from that study the extent to which $^{11}C(^1D)$ atoms might undergo 1,2-addition across the double bond of ethylene as shown in reaction (2). The resultant cyclopropylidene radical requires intermolecular abstraction or addition processes of uncertain efficiencies to give stable products which could also be formed by other reaction channels in the reaction system.

Because of this, buta-1,3-diene was selected as a model reactant since the vinyl cyclopropylidene radical generated from 1,2-addition of the carbon atom could undergo intramolecular addition or rearrangement processes to give stable products. For example, the unbounded electrons of vinyl cyclopropylidene could interact with the remaining π-bond in the radical to form [^{11}C]bicyclopent-2-ene, reaction (3). Bicyclopent-2-ene will isomerize to cyclopentadiene, reaction (4), however, with an activation energy of 26.9 ± 3 kcal mol^{-1}† and a half-life, at 24 °C, of *ca.* 4 h.[2]

In the irradiation of a 1 atm buta-1,3-diene gas target with a 33 MeV proton beam to generate carbon-11 *via* the $^{12}C(p, pn)^{11}C$ nuclear transformation, both the thermal heating of the target gas and the excess of translational energy carried into the reaction co-ordinate by the carbon atom should be sufficient to cause complete [^{11}C]bicyclopent-2-ene isomerization.

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† 1 kcal = 4.18 kJ.

$$^{11}C: * \quad + \quad CH_2=CH_2 \quad \longrightarrow \quad CH_2=^{11}C=CH_2 \quad (1)$$

$$^{11}C: \quad + \quad H_2C=CH_2 \quad \longrightarrow \quad \text{(2)}$$

$$^{11}C: \quad + \quad \longrightarrow \quad \longrightarrow \quad (3)$$
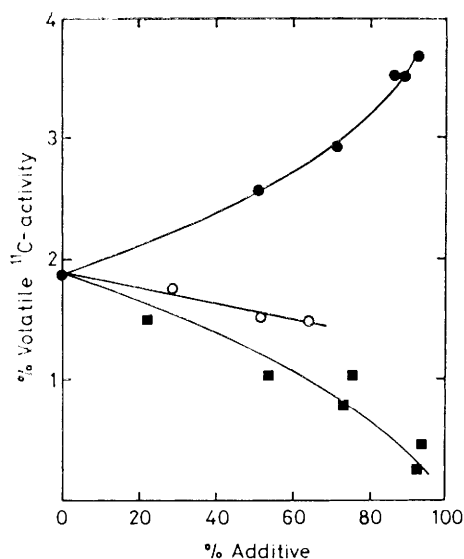
$$\longrightarrow \quad (4)$$

Figure 1. Effect of additives on the formation of [^{11}C]cyclopentadiene from the reaction of recoil ^{11}C atoms with buta-1,3-diene. Neon-moderated system, ●; oxygen-scavenged system, ○; xenon-moderated system, ■.

Products arising from the reactions of recoil ^{11}C-atoms with buta-1,3-diene were analysed using standard radio-gas chromatography. Product yields were expressed as percent volatile ^{11}C-activity. This comprised the total ^{11}C-activity present in the gas phase as stable volatile products. The total volatile ^{11}C-activity accounted for 75% of the total carbon-11 produced in the vessel. The remainder was accounted for as ^{11}C-labelled non-volatile polymer on the vessel walls.

The two major ^{11}C-labelled products observed in the present buta-1,3-diene system were [^{11}C]acetylene and [^{11}C]vinylallene. These are analogous to the [^{11}C]acetylene and [^{11}C]allene produced as major products in the ethylene system.[1,3] [^{11}C]Acetylene results from dissociation of the primary reaction adducts formed. C–H and C=C insertion mechanisms can be invoked to account for the [^{11}C]vinylallene produced in the buta-1,3-diene system similar to the mechanisms discussed for [^{11}C]allene formation from the ethylene system.[1]

As expected, [^{11}C]cyclopentadiene was observed in the carbon-11 product spectrum from the buta-1,3-diene system and not [^{11}C]bicyclopent-2-ene. A yield of 1.8% was measured for [^{11}C]cyclopentadiene from pure buta-1,3-diene samples. This yield was monitored as a function of the molar concentration of neon moderator, oxygen scavenger, and xenon moderator, relative to buta-1,3-diene, to determine the effects of energetics and electronic spin state on the ability of carbon atoms to undergo π-addition. The results from these studies are illustrated in Figure 1.

The following observations are made from the above experimental results. (i) The [^{11}C]cyclopentadiene yield doubles when 90% neon is added as an efficient translational energy moderator.[4] Such an increase indicates that thermal carbon-11 atoms are involved in the π-addition mechanism leading to the [^{11}C]cyclopentadiene formation. The fact that only a 1.8% volatile ^{11}C yield was obtained for this product for pure buta-1,3-diene samples suggests that the majority of the carbon-11 species react as translationally hot species. (ii) The [^{11}C]cyclopentadiene yield is essentially unchanged on addition of 30% oxygen which is very effective in the removal of $^{11}C(^3P)$ atoms.[5] On the other hand, its observed yield was drastically decreased to ca. zero through enhanced $^{11}C(^1D)$-to-$^{11}C(^3P)$ transitions on addition of 90% xenon as an electron spin converter. Xenon is 10^5 times more efficient than neon in inducing this transition.[6] It is apparent from both of these studies that only $^{11}C(^1D)$ atoms are involved in the generation of [^{11}C]cyclopentadiene.

Although experimental findings indicate that the precursors of [^{11}C]cyclopentadiene are likely to be thermal $^{11}C(^1D)$ atoms, mechanisms other than the π-bond addition process shown in reactions (3) and (4) could be considered. C–H insertion with

subsequent intramolecular addition or simultaneous 1,4-π bond addition by the carbon-11 atom are two possible channels. Previous studies have indicated, however, that insertion of $^{11}C(^1D)$ atoms (whether thermal or energetic) into a C–H bond of ethylene to produce [1-^{11}C]allene did not occur.[1] Also, simultaneous 1,4-addition of $^{11}C(^1D)$ atoms to buta-1,3-diene should be sterically less favoured, especially since the most stable conformation for buta-1,3-diene is its trans-form. By deduction, the 1,2-π bond addition process is likely to be the most feasible mechanism.

In the light of the results from the present work and the results from the previous study[1] it seems apparent (i) that $C(^1D)$ will preferentially attack the carbon–carbon double bond over a C–H bond of a C_n olefinic substrate to produce C_{n+1} products, (ii) that translationally hot $C(^1D)$ will undergo direct insertion into the double bond, and (iii) that thermalized $C(^1D)$ will add across the double bond.

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