

## Reaction of Energetic $^{11}\text{C}(^1\text{D})$ Atoms with Ethylene by Double-bond Insertion

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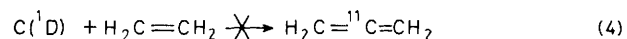
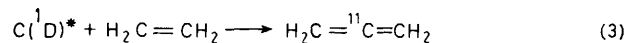
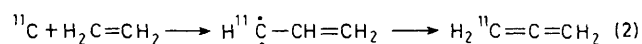
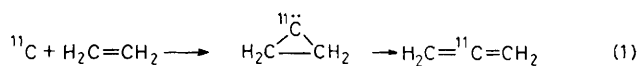
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Energetic  $^{11}\text{C}(^1\text{D})$  atoms insert into the double bond of ethylene to yield [2- $^{11}\text{C}$ ]allene, while the corresponding reaction with thermalized  $^{11}\text{C}(^1\text{D})$  atoms will not proceed; on the other hand,  $^{11}\text{C}(^3\text{P})$  atoms undergo both double bond and C-H insertion to yield [2- $^{11}\text{C}$ ]- and [1- $^{11}\text{C}$ ]allenes, respectively.

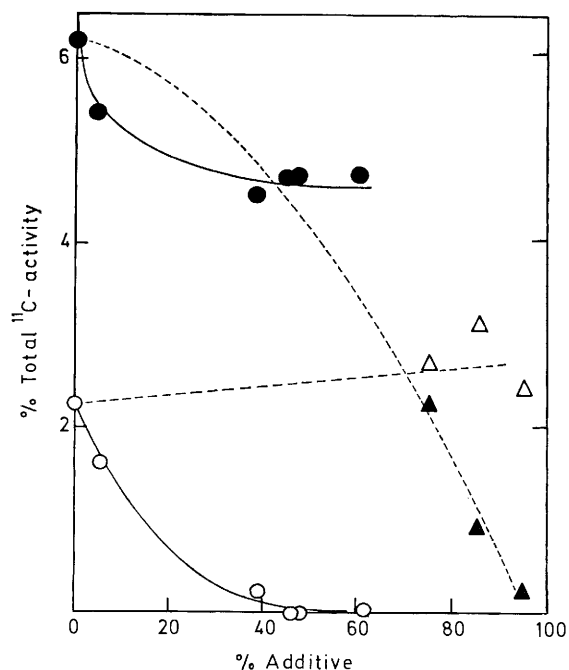
Past studies in carbon atom chemistry have used techniques such as nuclear transformation, thermal evaporation, thermal decomposition, and photolytic decomposition to generate the atomic species.<sup>1</sup> Known chemical interactions of carbon atoms with hydrocarbons include C-H insertion, double bond addition, and H-abstraction. The reactions of recoil carbon-11 atoms with ethylene were proposed to yield [2- $^{11}\text{C}$ ]allene through a cyclopropylidene intermediate generated by  $\pi$ -bond addition (reaction 1); and to yield [1- $^{11}\text{C}$ ]allene by C-H insertion (reaction 2).<sup>2</sup> Marshall *et al.*<sup>2</sup> degraded the [ $^{11}\text{C}$ ]allene in this system and observed 66% of [2- $^{11}\text{C}$ ]allene. Also, Mullen *et al.*<sup>3</sup> photolysed [2- $^{14}\text{C}$ ]suboxides in ethylene and observed 92% of [2- $^{14}\text{C}$ ]allene. However, the question of whether  $\text{C}(^1\text{D})$  or  $\text{C}_2\text{O}$  is the reactive species involved in the latter system remains unresolved.

In the present study, a novel degradation method has been established which includes the heterogeneous oxidation of [ $^{14}\text{C}$ ]acetone (derived from the acidic hydrolysis of [ $^{14}\text{C}$ ]allene) by potassium permanganate at elevated temperatures in a flow system. [ $^{14}\text{C}$ ]Acetone in the form of  $(\text{CH}_3)_2^{14}\text{CO}$  and



( $^{14}\text{CH}_3$ )<sub>2</sub>CO was employed. Under these oxidative conditions, the carbonyl carbon of acetone can be quantitatively oxidized to carbon dioxide while the methyl carbons are oxidized only to formaldehyde and formic acid.

This oxidative degradation method was used to study the effect of oxygen and neon additives on the reactions of  $^{11}\text{C}$  atoms with ethylene to produce [2- $^{11}\text{C}$ ]allene. In pure ethylene samples, an average of  $73.8 \pm 4.22\%$  [2- $^{11}\text{C}$ ]allene was obtained, in fair agreement with earlier results. This value increased to 100% with the addition of 40 mol % of oxygen as a scavenger, and decreased to 6% with the addition of



**Figure 1.** Effect of additives on the formation of [ $^{11}\text{C}$ ]allene from the reaction of recoil  $^{11}\text{C}$  atoms with ethylene. Oxygen-scavenged systems: ● [ $2\text{-}^{11}\text{C}$ ]allene; ○ [ $1\text{-}^{11}\text{C}$ ]allene; neon-moderated systems: ▲ [ $2\text{-}^{11}\text{C}$ ]allene; △ [ $1\text{-}^{11}\text{C}$ ]allene.

95 mol % of neon as a moderator. The corresponding absolute yields from these studies are illustrated in Figure 1. Besides the data displayed in Figure 1, when neon was added to well scavenged ethylene samples (ethylene: oxygen = 1.5:1) the 4.7% total  $^{11}\text{C}$  activity yield of [ $2\text{-}^{11}\text{C}$ ]allene decreased drastically to ca. 0 without a noticeable increase in the yield of [ $1\text{-}^{11}\text{C}$ ]allene.

The above experimental findings point to the following conclusions. (i) Energetic  $^{11}\text{C}(\text{D})$  carbon atoms insert into

the double bond of ethylene to yield [ $2\text{-}^{11}\text{C}$ ]allene (reaction 3) while the corresponding insertion by thermal  $^{11}\text{C}(\text{D})$  atoms will not proceed (reaction 4). This was shown by the persistence of [ $2\text{-}^{11}\text{C}$ ]allene in the high oxygen scavenged system and by the sharp decrease in C-2-labelling with high neon moderation. (ii) Insertion of  $^{11}\text{C}(\text{D})$  atoms (whether thermal or energetic) into a C-H bond of ethylene, although it may occur, does not produce [ $1\text{-}^{11}\text{C}$ ]allene, as shown by the essential absence of [ $1\text{-}^{11}\text{C}$ ]allene in the high oxygen scavenged samples with and without neon moderation. (iii)  $^{11}\text{C}(\text{P})$  atoms will undergo both double-bond and C-H insertions as shown by the diminished yields of both [ $1\text{-}^{11}\text{C}$ ]allene and [ $2\text{-}^{11}\text{C}$ ]allene in high oxygen scavenged ethylene samples. However, the present work does not deny the possibilities that  $^{11}\text{C}(\text{D})$  will undergo C-H insertion in the ethylene system to yield alternative products,<sup>4</sup> or that a distinct  $\pi$ -bond addition occurs with thermal carbon atoms to generate radical intermediates which produce larger hydrocarbon products.<sup>2</sup>

This research was kindly supported by the U.S. Department of Energy through the Brookhaven National Laboratory and through the Texas A&M Research Foundation.

Received, 6th October 1981; Com. 1179

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