# Reaction Intermediates in the Chemistry of Recoil Carbon Atoms

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ENERGETIC carbon atoms, produced by nuclear recoil, react with simple hydrocarbons to form acetylene, and ethylene, in high yields. Upon addition of oxygen scavenger, carbon monoxide is also formed because the carbon atoms reaching thermal energies react preferentially with oxygen.[1] The mechanism currently suggested for the initial step in such reactions involves insertion of the carbon atom into carbon–hydrogen bonds to form carbene intermediates.[2] Pressure-dependence studies were initiated to study the single collisional deactivation of such intermediates.[3]

In this work the $^{12}C(p,pn)^{11}C$ reaction was used to produce carbon atoms utilizing the 1—3 Gev proton beam of the Brookhaven Cosmotron. The total induced activity was monitored by mounting polyethylene foils on the reaction tanks and statically counting the activity induced in those foils. A correlation between the total induced activity and total gas-phase activity was necessary to distinguish true pressure trends from wall effects. The products formed in the irradiated samples were analysed by conventional radio-gas-chromatographic techniques.[4,5] The pressure trends observed for the scavenged cyclopropane system ($4\frac{1}{2}\%$ oxygen scavenger) where acetylene is the only major hydrocarbon product[1] are seen in Figure 1. The percentage of product is the total activity as product relative to the total gaseous activity. The recoil loss

$$\left(1 - \frac{\text{gaseous activity}}{\text{total induced activity}} \times 100\right),$$

at the various pressures used is shown in Figure 2.

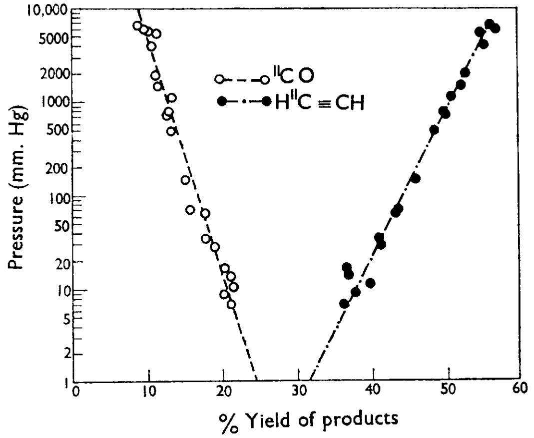


FIGURE 1. *Pressure trends in the cyclopropane–$4\frac{1}{2}\%$ oxygen system*

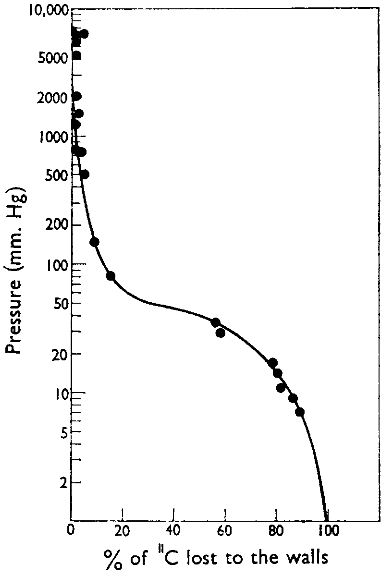


FIGURE 2. *Recoil loss in the cyclopropane–$4\frac{1}{2}\%$ oxygen system*

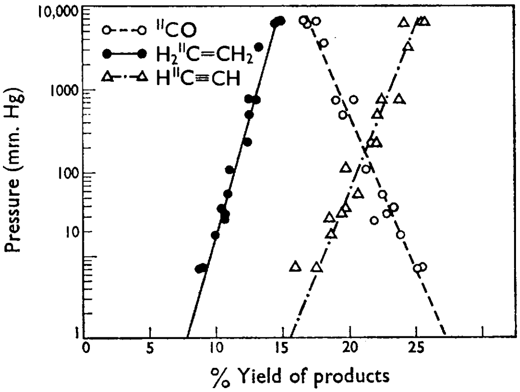
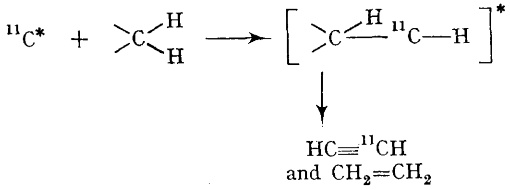


FIGURE 3. *Pressure trends in the propane–$4\frac{1}{2}\%$ oxygen system*

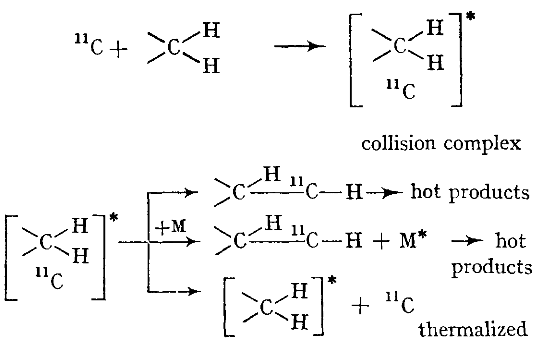
Comparison of Figures 1 and 2 shows that the same pressure trends are observed in regions of high recoil loss as in those of low recoil loss, showing that the trends in Figure 1 are true pressure effects and not associated with a wall effect. Similar pressure trends are observed in scavenged propane (Figure 3), methane, and neopentane systems. In all cases the effects are the same in high and low recoil loss regions. In these latter systems ethylene is also a major product and the ethylene pressure trend almost parallels that of acetylene.

Such pressure effects cannot be explained by the unmodified existing model of carbon atom insertion, *i.e.*,



Here it would be expected that the intermediate could be stabilized by collisional deactivation; this would show a pressure dependence opposite to that observed. Collisional stabilization or decomposition of an excited acetylene molecule would explain the observed acetylene trends but it is impossible to rationalize the ethylene and acetylene trends with such a model.

A model which is consistent with these results involves collision of an excited carbon atom leading first to a collision complex, where partial energy equilibration between the attacking species and the hydrocarbon occurs.



This collision complex can decompose to an excited hydrocarbon molecule and a thermalized carbon atom (which has more probability of reacting with oxygen than the original carbon atom) or be stabilized to a true carbene intermediate which is the precursor of the final products. As the pressure increases the number of complexes undergoing stabilization increases so the percentage of hydrocarbon product increases. Similarly the number of thermalized carbon atoms decrease and so the percentage of carbon monoxide decreases.

The pressure dependence is caused by the stabilization of a collision complex, and as the collisional frequency is very similar from one hydrocarbon to another the trends should be, and are, very similar.

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