The Reactivity of Thermal Carbon Atoms in the Gas Phase

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CARBON atoms were produced by decomposing [2-^{14}C]carbon suboxide in a discharge flow system. Helium was used as a carrier gas, and the discharge was maintained with a microwave resonance cavity. Reactants were added downstream of the cavity in times that varied from 5×10^{-3} to 6×10^{-2} sec. after an intermediate left the cavity. This minimum time allows the carbon atoms to undergo about 10^6 deactivating collisions at the pressures used (~6 cm. Hg). In addition, it allows them to be in one of the low-lying electronic states. Product analysis was performed using conventional radio-gas-chromatographic techniques,[1,2] the sensitivity being such that 0·033% of the carbon suboxide used in an experiment could be detected in a product peak.

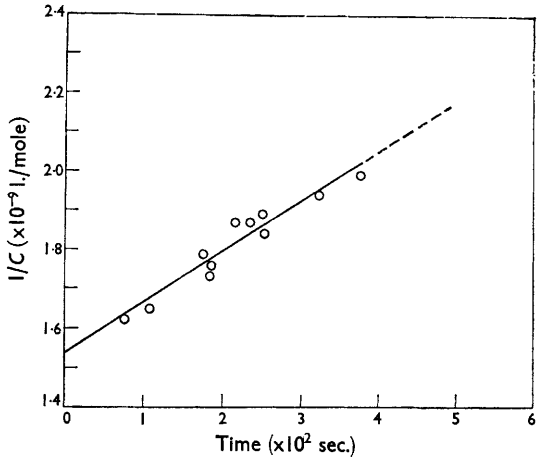
The rate of the carbon–carbon atom recombination reaction was determined by adding an excess of oxygen ($C:O_2 = 1:750$) at different points downstream of the cavity (*i.e.* different recombination times) and measuring the free carbon that has not recombined by the amount of carbon monoxide produced.[3] The Figure is a standard second-order rate plot for an initial carbon atom concentration, C_0, of $6{\cdot}5 \times 10^{-10}$ moles/l. The rate constant was thus obtained in the usual way. Experiments with various values of C_0 gave consistent second-order rate constants; whereas k values calculated for other orders varied with C_0. As no carbon activity appeared on the walls of the recombination tube we assumed negligible contribution from the reaction:

$$C + \text{wall} \rightarrow C_{\text{polymer}}$$

As the carbon atom reaction $C + C \longrightarrow C_2$ proceeds towards higher carbon atom consumption than shown in the Figure, reactions of the type $C_x + C \rightarrow C_{x+1}$ begin to compete for the remaining carbon atoms.

The rates of other carbon atom reactions relative to the recombination reaction were

determined by adding known amounts of reactants to the carbon atom flow. Under these conditions no products were obtained upon the addition of hydrogen, methane, ethylene, or acetylene and so only maximum values could be given for the



FIGURE

Rate plot for carbon atom recombination

rates of these reactions. The values obtained directly and those inferred from experiments at room temperature were:

$$k(C + C) \sim 1{\cdot}3 \times 10^{10} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k(C + O_2) \sim 1{\cdot}5 \times 10^{9} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k(C + H_2) < 4{\cdot}2 \times 10^{3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k(C + CH_4) < 3{\cdot}8 \times 10^{4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k(C + CH_2{=}CH_2) < 3{\cdot}8 \times 10^{4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

$$k(C + CH{\equiv}CH) < 3{\cdot}8 \times 10^{4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

The very high reactivity of carbon atoms in the recombination reaction, which occurs at least every fifth collision,[4] points to the carbon atoms formed being in the ground electronic state. The reaction:

$$C(^3P) + C(^3P) \rightarrow C_2(x^1\Sigma^+g)$$

is exothermic by 6·36 ev/mole.[5] This amount of energy can be absorbed if the carbon dimer is formed in a high electronic state.[5] The recombination reactions of the excited carbon atoms (^1D or ^1S states) would be exothermic by 9·0 and 11·76 ev/mole respectively, and this amount of energy cannot be taken up as electronic excitation.

This work shows that thermal gas-phase ^3P carbon atoms have low activity with hydrocarbons, a fact that is to be contrasted with the results of other workers,[6-8] who have studied the reactions of carbon atoms in various systems where an excess of energy is given to the reactant, as well as to the carbon-producing species.

If our experiments were performed so that hydrogen was also running through the discharge, forming hydrogen atoms, up to 38% of the available carbon reacted to form products, the major ones being acetylene and methane. The reactions are presumably (*cf.* ref. 9):

$$C + H \rightarrow CH$$

$$CH + H_2 \rightarrow CH_2 + H$$

$$CH_2 + H_2 \rightarrow CH_4$$

$$CH + CH \rightarrow CH{\equiv}CH$$

$$C_2 + 2H \rightarrow CH{\equiv}CH$$

Products were also formed when radicals produced from hydrocarbons by discharge were reacted with carbon atoms.

The high reactivity of carbon atoms with radicals as compared with hydrocarbons demonstrated by this work indicates that evaluation of results of any carbon atom studies must take into account not only the excitation state of the carbon atom but also the detailed composition and energy content of the substrate in which the carbon atom finds itself.

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