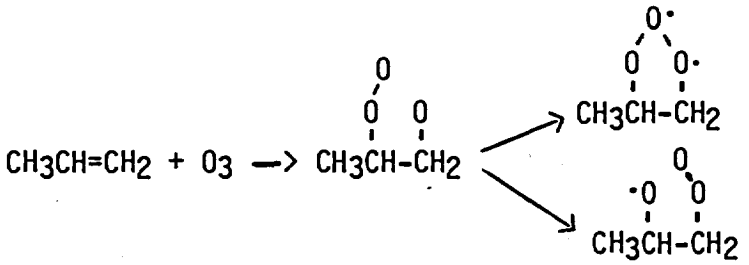
produces an unstable intermediate, which may decompose by several pathways (Niki, 1978; O'Neal and Blumstein, 1973). For propylene, for example, the initial step in the reaction with O_3 is believed to be:



(59)

Subsequent decomposition of the products leads to a variety of free radicals and stable products, including aldehydes and ketones (Herron and Huie, 1977; Niki et al., 1977). The mechanisms of ozone-olefin reactions are still under considerable study, although most of the potential paths have been delineated.

The reaction of olefins with atomic oxygen plays a minor role in olefin consumption and radical and product formation. Again, for propylene the reaction is:

$$CH_3CH{=}CH_2 + O(^3P) \longrightarrow CH_3CH_2 + HCO, \qquad (60a)$$

or

$$\longrightarrow CH_3CO + CH_3, \qquad (60b)$$

or

$$\longrightarrow CH_3CH_2CHO. \qquad (60c)$$

The mechanism of photooxidation of aromatic species in the atmosphere is perhaps the area of greatest uncertainty in atmospheric hydrocarbon chemistry. The principal reaction of aromatics is with the hydroxyl radical (Hendry, 1978; Perry et al., 1977). For aromatic-OH reactions, the initial step can be either addition to or abstraction from the aromatic ring. The free radical addition products may then react, most likely with either O_2 or NO_2, leading to the cresols or nitrotoluenes, respectively. The abstraction route probably leads to benzaldehyde or ring fragmentation. The mechanism of aromatic-hydroxyl radical reactions is yet to be clarified.