The alkyl radicals will rapidly add O_2 to form the corresponding peroxyalkyl radicals, e.g.,

$$CH_3CH_2CH_2CH_2 + O_2 + M \longrightarrow CH_3CH_2CH_2CH_2O_2 + M, \qquad (46)$$

(subsequently the third body M will not be indicated). A reaction of substantially lesser importance is with oxygen atoms,

$$CH_3CH_2CH_2CH_3 + O(3P) \xrightarrow{O_2} HO + CH_3CH_2CH_2CH_2O_2, \qquad (47a)$$

and

$$\xrightarrow{O_2} HO + CH_3CH_2\overset{OO}{C}HCH_3. \qquad (47b)$$

The importance of both the HO and $O(^3P)$ reactions with alkanes is the generation of the peroxyalkyl radical RO_2, which plays a substantial role in the conversion of NO to NO_2. Rate constants for alkane reactions are summarized by Baulch et al. (1980). The atmospheric chemical reactions involving olefins have been widely studied (Demerjian et al., 1974; Carter et al., 1979; Niki, 1978). The most important reactions in which olefins participate are with HO radicals, ozone, and atomic oxygen, in that order. The reaction of HO with an olefin, such as propylene, may proceed by addition of OH to the double bond or by abstraction of an H-atom from the olefin. For propylene, for example, the reaction paths with HO are:

$$CH_3CH = CH_2 + HO \longrightarrow CH_3CHCH_2OH, \qquad (48a)$$

$$\longrightarrow CH_3\overset{OH}{C}HCH_2, \qquad (48b)$$

$$\longrightarrow CH_2CH = CH_2 + H_2O. \qquad (48c)$$

In each case the free radical product will quickly react with O_2 to produce a peroxyalkyl radical that is capable of converting NO to NO_2.

Ozone-olefin reactions are a source of free radicals and stable products in air pollution chemistry. The initial attack of O_3 on an olefin