Peroxyacyl nitrates have been recognized as important components of photochemical air pollution (U.S. EPA, 1978). Peroxyacetyl nitrate (PAN) exists in equilibrium with the peroxyacyl radical and NO_2:

$$CH_3\overset{O}{\overset{\parallel}{C}}OO + NO_2 \Longleftrightarrow CH_3\overset{O}{\overset{\parallel}{C}}OONO_2. \quad (71)$$

There exists a competition between NO and NO_2 for the peroxyacyl radical through:

$$CH_3\overset{O}{\overset{\parallel}{C}}OO + NO \Longleftrightarrow CH_3\overset{O}{\overset{\parallel}{C}}O + NO_2. \quad (72)$$

The acetyl radical will rapidly decompose as follows:

$$CH_3\overset{O}{\overset{\parallel}{C}}O \longrightarrow CH_3 + CO_2, \quad (73)$$

followed by:

$$CH_3 + O_2 \longrightarrow CH_3O_2, \quad (40)$$

$$CH_3O_2 + NO \longrightarrow CH_3O + NO_2, \quad (41)$$

$$CH_3O + O_2 \longrightarrow HCHO + HO_2, \quad (42)$$

$$HO_2 + NO \longrightarrow OH + NO_2. \quad (43)$$

Thus, PAN chemistry is intimately interwoven in the NO to NO_2 conversion process. Rate constants for reactions 71 and 72 have recently been reported by two groups of investigators (Cox and Roffey, 1977; Hendry and Kenley, 1977).

The chemistry of the oxides of nitrogen in a hydrocarbon-containing atmosphere can be summarized as follows: the major observed phenomenon in the system is conversion of NO to NO_2 and formation of a variety of nitrogen-containing species, such as nitrites and nitrates. The conversion of NO to NO_2 is accompanied by accumulation of O_3. NO_2 serves both as initiator and terminator of the chain reactions that result in conversion of NO to NO_2 and buildup of O_3. Termination of the chain reactions leads to nitric acid