

reported value for NO_2 are frequently used. A recent review of theoretical estimates of photolytic rate constants in the lower troposphere by Demerjian, Schere and Peterson (1980) indicates that for species such as NO_2 , HONO , H_2O_2 , O_3 , and formaldehyde, extensive experimental determinations of absorption cross sections and quantum yields are fairly reliable. However, since cross section and quantum yield data for higher aldehydes, alkyl nitrites and other carbonyl compounds are much less well characterized, these photolysis rate constants are subject to a large uncertainty. Of course, even if absorption cross sections and quantum yields could be determined accurately for all photo-sensitive species, uncertainties in atmospheric photolysis rate constants would still exist, as meteorological conditions, clouds, dust, and aerosols cause unknown variances in actinic irradiance.

Whereas rate constants in the inorganic portion of the mechanism are known fairly well, many more uncertainties, both in reaction rate constants and products, are associated with the organic reaction steps. Still to be determined are product distributions and reaction rate constants for the initial steps of the reactions of OH and hydrocarbon species, the largest uncertainties lying in the routes of the various radical species produced. For example, although rate constants for alkane-OH reactions are well established, the ratio of internal to external abstraction for all alkanes is not known. Addition to O_2 to form peroxyalkyl (RO_2) radicals can be considered as the sole fate of the alkyl radicals first produced in alkane-OH reactions, but after the formation of alkoxy radicals through the conversion of NO to NO_2 , the reaction mechanism becomes uncertain. Alkoxy radicals can decompose, react with O_2 , isomerize, or react with NO or NO_2 , with the importance and rate of each reaction path depending on the nature of the alkoxy group. Even for the most studied of the alkane-hydroxyl radical reactions, the relative rates between decomposition, isomerization, and reaction with O_2 , NO, and NO_2 for alkoxy radicals have not been measured, but must be estimated (Baldwin et al., 1977).

Less well understood than alkane reaction mechanisms are olefin oxidation processes, primarily by HO. Olefin-hydroxyl radical reactions may proceed by addition or abstraction. For smaller olefins, the addition path predominates. However, the abstraction fraction increases with the size of