Mn(II) and Fe(III)] and carbon catalyze the oxidation of dissolved SO_2 to form H_2SO_4 in the absence of oxidants. The aqueous-phase may be acidified by the reaction of dissolved HNO_2 with oxidants, but since limited data exists on ambient HNO_2 concentration levels, the importance of this reaction is unknown. The relative importance of the gas-phase and the aqueous-phase pathways for various geographical regions has not been established; but there are indications that the aqueous-phase pathway is dominant for H_2SO_4 formation. The relative importance of the pathways for HNO_3 formation is not known, but it appears that the overall HNO_3 formation rate is greater than 5 times that for H_2SO_4.

4.3.1 The Photochemical Oxidation Cycle

Of the four major acidification (oxidation) pathways shown in Figure 4.1, the first three depend upon free radicals produced directly and indirectly in the photochemical oxidation cycle for polluted atmospheres. This cycle (Figure 4.2) is governed by the following basic features. Free radical attack on atmospheric volatile organic compounds (VOC) is inititated by a select group of compounds which are for the most part activated by sunlight. Formaldehyde and nitrous acid, in particular, show high potential as free radical initiators during the early morning sunrise period. After the initial free radical attack, the VOC's decompose by various paths resulting in the production of peroxyl radical species (HO_2, RO_2, $R'O_2$, etc.) and partially oxidized products which in themselves may be photoactive radical-producing compounds (R is a fragment of an organic molecule). The peroxyl radicals react with NO, converting it to NO_2, and in the process produce hydroxyl/alkoxyl radical species (HO, RO, R'O, etc.). Alkoxyl radicals can be further oxidized, forming additional peroxyl radicals and partially oxidized products, thereby completing the inner cylical loop reaction process illustrated in Figure 4.2; or they may attack the VOC pool (this is the major path for hydroxyl radical) present in the polluted atmosphere, thereby completing the outer loop