4.3.2 Free Radical (Gas Phase) Oxidation

The features of the free radical oxidation of SO_2 are presented in Table 4.1.

Based on limited rate constant data for the SO_2-free radical reactions, Calvert[3] determined from computer model simulations that the hydroxyl radical dominated the rate of SO_2 oxidation in the clean troposphere, while in polluted atmospheres the rate of SO_2 oxidation showed equivalent contributions from the hydroxyl, hydroperoxyl (HO_2) and methylperoxyl (CH_3O_2) radicals. Figure 4.3 depicts the estimated time dependent rates of SO_2 oxidation by free radical species in a polluted air mass. Typical rates of SO_2 oxidation were of the order of 1.5% per hour and 4.0% per hour for clean and polluted atmospheres, respectively, during July at mid-northern latitudes. The major difference in these rates is a result of higher concentration levels of free radicals in the hydrocarbon-rich polluted atmospheres. In a similar manner, Altshuller[4] predicted the rates of homogeneous oxidation of sulfur dioxide to sulfate in the clean troposphere using concentration predictions of the pertinent free radicals from a two dimensional global model by Fishman and Crutzen[5]. A sample result from this study showing the altitudinal, latitudinal and seasonal dependence of the average diurnal rate of SO_2 oxidation in the clean troposphere is presented in Figure 4.4. For the polluted troposphere, the rates shown in Figure 4.4 may be up to about a factor of 3 greater due to the higher HO_2 and RO_2 concentrations. Altshuller has concluded that the gas-phase oxidation rate of SO_2 is important for low latitudes at all seasons, and at high latitudes only during the summer.

Recent laboratory measurements[6,7,8] suggest that the rate of reaction of SO_2 with HO_2 may not be as great as estimated by Calvert[3]. But even these results may not be totally conclusive since preliminary experimental work by Calvert has indicated that the