4.3.3 Aqueous-phase Oxidation

The relative magnitudes of the contribution of gas-phase and aqueous-phase formation of H_2SO_4 vary as a function of season. At southern latitudes for all seasons it is likely that the gas-phase photooxidation pathway is important. At northern latitudes for all seasons, it is likely that the aqueous phase SO_2 oxidation pathways (wet particles, fogs, clouds, precipitation) is important and in the winter is dominant. At this time, the significance of the aqueous phase NO_2 oxidation pathways to form HNO_3 is not known. The knowledge of aqueous oxidation rates of dissolved SO_2 is barely adequate for simple (clean) systems, inadequate for N-oxides and N-oxy acids systems, and practically non-existent for complex sulfur dioxide/N-oxides/N-oxy acids/organic/catalyst/oxidizer systems. Studies of these systems are made difficult by the need for high-purity reagents, the type of chemical reactors required, and the lack of sensitive instrumentation/methods to determine the reaction rates at the low pollutant concentrations (ambient values).

The dissolved SO_2 oxidation reaction rate expressions (see Table 4.1) for H_2O_2, O_3, and HNO_2 are known and are non-linear. Each of the three rates depends upon the liquid water content (LWC) of the atmosphere, which leads to gross non-linearity in the H_2SO_4 formation rate due to its extreme spatial-temporal variation in the atmosphere over short time periods. The H_2O_2 reaction rate expression has first order dependence on the H_2O_2 and SO_2 concentrations in the gas phase and has no dependence on the pH of the water until the pH declines to about 2. Thus, this reaction in cloud and raindrops will continue to acidity atmospheric water at a constant reaction rate until either the gas-phase H_2O_2 or the SO_2 is completely consumed. The indications[9,10] are growing that this reaction is the important one for acidifying rainfall and atmospheric particles. It is estimated that this reaction accounts for about 75% of the H_2SO_4 formed in the atmosphere[11].