of laboratory and field data as well as theoretical studies, indicated that SO_2 oxidation may proceed through both gas and liquid phase reactions. The oxidation of SO_2 in the atmosphere is of considerable importance, in that it represents a major pathway for particle production through the formation of sulfates. Homogeneous gas phase reactions are by far the most extensively studied and best understood quantitatively.

Gas-Phase Chemical Reactions of SO_2

The homogeneous gas-phase chemistry of oxidation in the clean and polluted troposphere is reviewed in this section. The status of our knowledge is presented for the elementary oxidation reactions of SO_2 and the importance of volatile organic and nitrogen oxides as generators of free radical oxidizers. This review will show that the photochemical oxidation of SO_2 is potentially a significant pathway for tropospheric sulfate formation. The three most important oxidizers of SO_2 are: (1) hydroxyl radical HO; (2) peroxyl radical, HO_2; and (3) methoxyl radical, CH_3O_2. At this time, only the reaction rate constant for HO is well established. The pathways of formation of the oxidizer radicals for the unpolluted troposphere can be explained in terms of the photochemistry of the NO-HC-CO-O_3 system. In polluted atmospheres, volatile organics and oxides of nitrogen act together to produce additional radicals and accelerate overall radical production. There is also evidence that a dark reaction among O_3, alkenes, and SO_2 is effective in oxidizing SO_2.

The elementary chemical reactions of SO_2 in air have been the subject of intense investigation. Studies prior to 1970 have been critically reviewed by Bufalini (1971), and more recently by Calvert et al. (1978). The review of Calvert et al. (1978) systematically examined the rate constants and significance of SO_2 elementary reactions known to occur in the troposphere; identified as generally unimportant reactions were: photodissociation, photoexcitation, reaction with singlet delta oxygen [$O_2(^1\Delta g)$], reaction with triplet oxygen atom [$O(^3P)$], reaction with ozone (O_3), reaction with nitrogen oxides (NO_2, NO_3, N_2O_5), reaction with tert-butylperoxyl radical [$(CH_3)_3CO_2$], and reaction with acetyl-peroxyl radical (CH_3COO_2). The only SO_2 reactions in the troposphere that were identified as important were those due to hydroxyl