

oxidizers of SO_2 are: (1) hydroxyl radical HO ; (2) peroxy radical, HO_2 , and (3) methoxy radical, CH_3O . 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-CH-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 .

2.3.3.1 Elementary Reactions - The elementary chemical reactions of SO_2 in air have been the subject of intense investigation. Studies prior to 1965 have been critically reviewed by Altshuller and 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 [$\text{O}_2(^1\Delta_g)$] reaction with oxygen atom [$\text{O}(^3\text{P})$] reaction with ozone (O_3), reaction with nitrogen oxides (NO_2 , NO_3 , N_2O_5), reaction with tert-butylperoxy radical [$(\text{CH}_3)_3\text{CO}_2$], and reaction with acetyl-peroxy radical (RCOO_2). The only SO_2 reactions in the troposphere that were identified as important were those due to hydroxyl radical (HO), peroxy radical