

reactions of SO_2 with CH_3O_2 may be accelerated by trace levels of NO . Therefore, in the theoretical estimates of SO_2 oxidation rates, by Calvert, and by Altshuller, only the hydroxyl radical portion of the contribution is now accepted as established, in view of these recent experimental rate constant determinations. This results in maximum established SO_2 oxidation rates of the order of 1.5% per hour for both clean and polluted atmospheres during July at mid-northern latitudes, a factor of 2.5 less than previous theoretical estimates for polluted atmospheres. The revised rate is equivalent to a diurnally averaged rate of the order of 0.4% per hour. However, field measurements of the rates of SO_2 oxidation indicate that maximum SO_2 oxidation rates of the order of 10% per hour (diurnally averaged rates of the order of 1-2% per hour) are typical of many atmosphere pollution scenarios, which suggests that aqueous-phase reactions are important.

Since the production of the oxidizing radicals HO , HO_2 , and RO_2 is a complex process that is dependent upon sunlight intensity and precursors, it follows that the gas-phase oxidation rate of SO_2 is non-linear. The adequacy of its representation as a linear process is dependent in a complex manner upon the transport time scale, the geographical distribution and type of sources, and the removal time scale.

There are potential pathways for radical production at night. These pathways involve the O_3 -olefin reaction to produce radicals that can oxidize SO_2 to H_2SO_4 . They also involve the formation of an NO_3 radical, which may participate in the formation of organic nitrates and HNO_3 . The radicals which have a direct photochemical dependence cannot be transported on a regional scale because of their very short lifetimes. Those radicals, which are produced through thermal reactions, may be transported regionally and the radicals may be present during the night.