

radical (HO), peroxy radical (HO₂), and methoxyl radical (CH₃O₂). The rate constants recommended by Calvert et al. (1978) for these three reactions are given in Table VII. More recent work is in conflict with the rate constants for HO₂ and CH₃O₂ that have been recommended by Calvert et al. (1978). Graham et al. (1979) and Burrows et al. (1979) have reported rate constants for the HO₂ reaction that are much lower than that recommended by Calvert et al. (1978); these more recent results are shown in Table VII. Also, Sander and Watson (1981) have reported a rate constant for the CH₃O₂ reaction that is much lower than that recommended by Calvert et al. (1978); that value is given in Table VII. The reasons for the discrepancies for these two rate constants are unknown, and there is no basis to recommend preferred values.

Although the dark reaction of SO₂ + O₃ is too slow to be important in the troposphere, the addition of alkenes greatly enhances the oxidation rate. The experimental work of Cox and Penkett (1971a,b, 1972) and McNelis et al. (1975) has been reviewed and reevaluated by Calvert et al. (1978). The reaction system is too complex to discuss here, but Calvert et al. (1978) report results of their calculations for total alkenes = 0.10 ppm, [O₃] = 0.15 ppm, and [SO₂] = 0.05 ppm; they estimated that the disappearance rate of SO₂ is 0.23 and 0.12% h⁻¹ at 50 and 100% relative humidity (25°C), respectively. The reaction mechanism for the O₃ + alkene + SO₂ system is not known, but studies by Niki et al. (1977) and Su et al. (1980) indicate that the reactive species may be the biradical, formed by the decomposition of the original molozanide.

The status of our knowledge of the gas-phase tropospheric oxidation reactions is:

1. Three reactions have been identified as being potentially important.
 - a. HO radical. The rate constant appears to be well established.
 - b. HO₂ radical. The rate constant is not well established.
 - c. CH₃O₂ radical. The rate constant is not well established.
2. The SO₂ + O₃ + alkenes reaction may be an important dark reaction.