

TABLE VII. Rate Constants for Hydroxyl, Peroxyl, and Methoxyl Radicals

Reaction	Second order rate constant, $\text{cm}^3\text{mole}^{-1}\text{s}^{-1}$	Source
$\text{HO} + \text{SO}_2 \rightarrow \text{HOSO}_2$ $\quad \quad \quad \rightarrow \text{H}_2\text{SO}_4$	$(1.1 \pm 0.3) \times 10^{-12}$	Calvert et al. (1978)
$\text{HO}_2 + \text{SO}_2 \rightarrow \text{HO} + \text{SO}_3$ $\quad \quad \quad \rightarrow \text{H}_2\text{SO}_4$	$>(8.7 \pm 1.3) \times 10^{-16}$	Calvert et al. (1978)
	$<1 \times 10^{-18}$	Graham et al. (1979)
	$\leq 2 \times 10^{-17}$	Burrows et al. (1979)
$\text{CH}_3\text{O}_2 + \text{SO}_2 \rightarrow \text{CH}_3\text{O} + \text{SO}_3$ $\quad \quad \quad \rightarrow \text{H}_2\text{SO}_4$	$(5.3 \pm 2.5) \times 10^{-15}$	Calvert et al. (1978)
	5×10^{-17}	Sander and Watson (1981)

In its simplest form the photochemical oxidation cycle in polluted atmospheres (which has been previously discussed) is governed by the following basic features. Free radical attack on atmospheric VOCs is initialized by a select group of compounds which are for the most part activated by sunlight. Formaldehyde and nitrous acid, in particular, show high potential as free radical initiators during the early morning sunrise period. After initial free radical attack, the VOCs decompose through paths resulting in the production of peroxy radical species (HO_2 , RO_2 , $\text{R}'\text{O}_2$, etc.) and partially oxidized products which in themselves may be photoactive radical-producing compounds. The peroxy radicals react with NO , converting it to NO_2 , and in the process produce hydroxyl/alkoxy radical species (OH , RO , $\text{R}'\text{O}$, etc.). Alkoxy radicals can be further oxidized, forming additional peroxy radicals and partially oxidized products, thereby completing the inner cyclical loop reaction chain process illustrated in Figure 5; or they may attack, as would be the major path for hydroxyl radical, the VOC pool present in the polluted atmosphere, thereby completing the outer loop reaction chain process. The resultant effect in either case is the conversion of NO to NO_2 with a commensurate oxidation of reactive organic carbon.