

The complex mixture of organic compounds present in the polluted atmosphere react at different rates depending upon their molecular structure, the result being varying yields of free radical species, ozone,  $\text{NO}_2$ , PAN and other partially oxidized organic products as a function of VOC composition and VOC- $\text{NO}_x$  levels.

Hydroxyl radical (HO) reactions seem to be the dominant gas-phase mechanism by which hydrocarbons, nitrogen dioxide and sulfur dioxide are consumed in the atmosphere (Niki et al., 1972; Demerjian et al., 1974; Calvert et al., 1978). Interestingly enough, this highly reactive transient species, quite contrary to its organic free radical counterparts, does not show appreciable change in concentration with atmospheric VOC and  $\text{NO}_x$  variation, a result readily explainable upon review of the free radical production and consumption sources. In the case of hydroxyl radicals, ambient concentration conditions which enhance its production tend to also consume the radical at an equivalent rate. The result is a faster cycling in the VOC- $\text{NO}_x$  oxidation chain (that is, increased chain lengths) but very little perturbation in the HO steady state concentration. In contrast, organic free radicals, mainly peroxy species, are consumed by alternate pathways which are less competitive and result in increased steady state concentration.

Applying this basic knowledge of the photochemistry of the lower atmosphere, Calvert et al. (1978) determined theoretical rates of  $\text{SO}_2$  oxidation via attack of various free radical species whose concentrations were estimated from computer simulations of the chemical reaction mechanisms (using the rate constants given in Table VII) for clean and polluted atmospheres.

Based on limited rate constant data for the  $\text{SO}_2$ -free radical reactions, Calvert determined that the hydroxyl radical dominated the rate of  $\text{SO}_2$  oxidation in the clean troposphere, while in polluted atmospheres the rate of  $\text{SO}_2$  oxidation showed equivalent contributions from hydroxyl, hydroperoxyl ( $\text{HO}_2$ ), and methylperoxyl ( $\text{CH}_3\text{O}_2$ ) radicals. Figure 6 depicts the estimated time dependent rates of  $\text{SO}_2$  oxidation by free radical species in a polluted air mass. Recent laboratory measurements suggest that the rate of reaction of  $\text{SO}_2$  with  $\text{HO}_2$  and  $\text{CH}_3\text{O}_2$  may not be as great as estimated by Calvert et al. (1978). Typical rates of  $\text{SO}_2$  oxidation were predicted to be of the order of