

smog. To understand the chemistry of the formation of oxidants in the polluted lower troposphere, it is necessary to consider the interactions that take place between the oxides of nitrogen and organic constituents. Several reviews of polluted atmospheric chemistry are available (Leighton, 1961; Stern, 1977; Seinfeld, 1975; Heiklen, 1976), as are detailed discussions of reaction mechanisms (Demerjian et al., 1974; Carter et al., 1979; Baldwin et al., 1977; Whitten and Hogo, 1977; Falls and Seinfeld, 1978), and rate constants (Baulch et al., 1980). In this section the chemistry of the oxides of nitrogen and organics in the lower polluted troposphere is briefly reviewed. The above-cited references should be consulted for more detail.

Most of the chemistry that occurs in a sunlight-irradiated polluted atmosphere involves the interaction of a variety of molecules, excited molecules and molecular fragments. These species include: hydrocarbons; organics such as aldehydes and ketones; the unexcited and first excited electronic states of the oxygen atom, triplet-P oxygen atoms [$O(^3P)$], and singlet-D oxygen atoms [$O(^1D)$]; ozone (O_3); nitrogen dioxide (NO_2); nitric oxide (NO); symmetrical nitrogen trioxide (NO_3); dinitrogen pentoxide (N_2O_5); hydroxyl radicals (HO); hydroperoxyl radical (HO_2); alkylperoxyl radicals (RO_2); acylperoxyl radicals $RC(O)O_2$; and less important species. In the formulas, R represents a methyl (CH_3), ethyl (C_2H_5), or another, more complex hydrocarbon radical. The paths by which these intermediates are formed and destroyed are important keys in explaining the chemical changes that occur in the polluted atmosphere.

The major portion of the total oxides of nitrogen emitted by combustion sources is nitric oxide (NO). The rate at which NO is converted to nitrogen dioxide (NO_2) through oxidation by molecular oxygen in air:



is proportional to the square of the nitric oxide concentration since two molecules of NO are required for the oxidation; it is, therefore, very sensitive to changes in nitric oxide concentration. Reaction 20 can be important in the vicinity of high NO emission sources in converting up to 25% of the total NO_x to NO_2 during the initial stages of dilution with air when the concentration of NO is still quite high. Reaction 20 is much too slow,