

6.1 CHEMISTRY OF THE OXIDES OF NITROGEN IN THE LOWER ATMOSPHERE

Solar radiation triggers a series of reactions in the atmosphere between gaseous organic molecules and nitrogen oxides, producing a wide variety of secondary pollutants. The totality of primary and secondary pollutants involved in these photochemical reactions is known as photochemical smog. To understand the chemistry of the oxides of nitrogen in the lower atmosphere, it is necessary to consider the interactions that take place between the oxides of nitrogen and organic constituents. Several reviews of atmospheric chemistry are available, 1-3 as are detailed discussions of reaction mechanisms 4-8 and rate constants.⁹ In this section the chemistry of the oxides of nitrogen in the lower atmosphere is briefly reviewed. The above-cited references should be consulted for more detail.

Most of the chemistry that occurs in a sunlight-irradiated urban atmosphere involves the interaction of a variety of unstable, excited molecules and molecular fragments that have only a transitory existence. These species include: 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); symmetrical nitrogen trioxide (NO_3); dinitrogen pentoxide (N_2O_5); hydroxyl radicals (HO); alkylperoxyl radicals (RO_2); acylperoxyl radicals $RC(O)O_2$; and less important species. In the formulas, R represents a