Laboratory Evidence of the NO₂-to-Precursor Relationships

In the previous section, the nature of chemical reactions involving oxides of nitrogen and hydrocarbons in the atmosphere was discussed. These reactions have traditionally been studied experimentally in laboratory vessels called smog chambers. These chambers characteristically employ radiation sources that closely approximate the UV portion of the solar spectrum as observed at the earth's surface and clean, chemically inert interior surfaces. It is believed that the chemical processes that take place in smog chambers are similar to those that take place in the atmosphere.

The presence of surfaces in a smog chamber may, however, be a source of difficulty in interpreting chamber results because of possible surface-catalyzed reactions or absorption of species on the walls. In addition, most chamber experiments have been conducted by initially injecting fixed amounts of reactants rather than simulating the continuous time-varying injection and dilution of reactants that characterize the ambient situation. Nevertheless, the behavior of irradiated mixtures of oxides of nitrogen and hydrocarbons in smog chambers has served as the foundation for our understanding of atmospheric chemical mechanisms.

Considerable effort has been devoted to the development of chemical reaction mechanisms that are capable of describing the processes observed in smog chambers (Demerjian et al., 1974; Carter et al., 1979; Baldwin et al., 1977; Whitten and Hogo, 1977; Falls and Seinfeld, 1978). Smog chambers have been used extensively to determine how concentrations of NO_X and other photochemical products respond to changes in the initial composition of nitrogen oxides and organics. The ozone/photochemical criteria document (U.S. EPA, 1978) discusses smog chamber evidence concerning the relationship between ozone/oxidant and the photochemical precursors. This section focuses on how NO₂ concentrations respond to changes in the input levels of organics and nitrogen oxides.

Several researchers have used smog chambers to investigate the dependence of nitrogen dioxide concentrations on the levels of precursor inputs: