

and organic nitrates. The nature of the system can be explained by considering its behavior as a function of the initial concentrations of  $\text{NO}_x$  and hydrocarbon in the irradiation of a static system, as well as the ratio of two reactants, i.e., the  $[\text{HC}]/[\text{NO}_x]$  ratio.

At low  $[\text{HC}]/[\text{NO}_x]$  ratios (usually ratios of less than about 1 to 2/1) the rate at which  $\text{NO}$  is converted to  $\text{NO}_2$  is influenced by the availability of organic compounds. Therefore, the effects of reducing organic compounds are to slow the conversion of  $\text{NO}$  to  $\text{NO}_2$ , thereby lowering the  $\text{NO}_2/\text{NO}$  ratio. When this occurs, a larger proportion of the  $\text{NO}$  that is converted to  $\text{NO}_2$  occurs through the reaction with ozone. This, then, has the overall effect of reducing the ozone buildup. If the oxidation of  $\text{NO}$  by organics is delayed sufficiently so that the sun has passed its zenith before significant amounts of  $\text{NO}_2$  are created, photodissociation of  $\text{NO}_2$  will be diminished and less ozone will accumulate on that date. At moderately high  $[\text{HC}]/[\text{NO}_x]$  ratios (usually greater than about 5 to 8/1), the greater availability of organic radicals means that all of these radicals are not consumed as rapidly in reactions with  $\text{NO}$ , and more reactions between the radicals and  $\text{NO}_2$  are able to occur. Thus, the amount of ozone formed and accumulated begins to become limited by the availability of  $\text{NO}_x$ , and becomes less sensitive to additional organic precursors. At very high  $[\text{HC}]/[\text{NO}_x]$  ratios (greater than about 20 to 30/1), ozone cannot accumulate because either the ozone is consumed by reaction with hydrocarbons,  $\text{NO}_x$  becomes unavailable due to reactions with free radicals, and radical-radical termination reactions occur which reduce oxygen atom and, hence, ultimate ozone concentration.

Identification of the nitrogen-containing products in atmospheric reactions has been under investigation for a number of years (Gay and Bufalini, 1971; Spicer and Miller, 1976; Pitts, 1977). In general, the most important gaseous nitrogen-containing products in the  $\text{NO}_x$ -organic system are nitric acid and PAN. As noted, reactions of  $\text{NO}$  and  $\text{NO}_2$  with free radicals produce, in addition to nitrous, nitric, and peroxy-nitric acids, a variety of organic nitrogen-containing species (Table IV). There currently exist important areas of uncertainty with regard to the formation of nitrogen-containing products in atmospheric reactions. The extent of formation and decomposition of peroxy-nitrates,  $\text{RO}_2\text{NO}_2$ , is unknown, and rate constants for the key reactions in the series,  $\text{RO}_2 + \text{NO}$ , are yet to be determined.