

Little is known about the existence and importance of peroxy nitrates other than HO_2NO_2 and PAN. It is presumed in the mechanism on which the results of Table VI are based that RO_2NO_2 thermally decomposes at a rate between those for HO_2NO_2 and PAN. Assessment of the importance of RO_2NO_2 as a sink for NO_x will depend on measurement of the rates of reactions 69 and 70.

In contrast to the other species of Table VI, nitric acid and alkyl nitrates apparently do not undergo appreciable decomposition reactions. Thus, these two species potentially serve as important atmospheric sinks for NO_2 . Both nitric acid and alkyl nitrates may remain in the gas phase or react with other atmospheric constituents, such as ammonia, to produce low vapor pressure species that have a tendency to condense on existing particles or homogeneously nucleate to form particles.

Figure 4 depicts the potential paths by which particulate nitrate species may be formed from NO and NO_2 . Path 1 involves the formation of gaseous nitric acid by reactions 27 and 38. Nitric acid concentrations resulting from these two reactions for the simulated smog chamber experiment have been given in Table VI. Comparisons of the individual rates of reactions 27 and 38 indicate that reaction 38 is the predominant route for gas-phase nitric acid formation under typical daytime conditions. Nitric acid vapor, once formed, may then react with NH_3 , a ubiquitous atmospheric constituent with both natural and anthropogenic sources, to produce ammonium nitrate, NH_4NO_3 (path 2), which at standard temperature and pressure, exists as a solid. Alternatively, the nitric acid vapor may be absorbed directly onto a particle (path 3), although thermodynamic and kinetic considerations favor reaction with NH_3 to form NH_4NO_3 as the path of conversion of gaseous nitric acid to nitrate in particulate form (Bradner et al., 1962; Morris and Niki, 1971; Stelson et al., 1979). Path 4 involves the direct absorption of NO and NO_2 into an atmospheric particle, a route that is likely for certain aqueous particles, particularly when accompanied by the absorption of ammonia (path 5) (Orel and Seinfeld, 1977). Path 6 depicts the formation of organic nitrates through reactions such as 67a, followed by absorption of these nitrates into particles. At present little is known about the existence or importance of mechanisms such as that depicted by Path 6.