ABSTRACT

Processes of relevance to the atmospheric chemistry e.g. of biogenic volatile organic compounds were investigated in this work. Nitrate radical kinetics, product schemes, and vapor pressures of some products were determined. The kinetics of NO_3 initiated reaction of some unsaturated alcohols, alkenes, *n*-alkylaldehydes, and hydroxynitrates were studied by the relative rate method. The analytical techniques used were solid phase micro extraction (SPME) coupled with gas chromatography and/or Fourier transform infrared spectroscopy (FTIR). Results from these kinetic studies revealed that NO_3 radical reaction can be a significant loss process under certain conditions such as dry and warm weather together with high concentration of NO_2 and O_3 during dark hours. Available structure activity relationships (SAR) fail to predict aldehyde greater than C_4 and hydroxy nitrate rate coefficients. The results for a series of unsaturated alcohols and the corresponding, structurally similar alkenes showed no influence on rate coefficients by -OH substitutens 2 or 3 carbon atoms away from the double bond.

A product study for some methyl butenols reacting with NO_3 radicals showed formation of formaldehyde, acetaldehyde, and nitrated carbonyl compounds. In particular, 2-methyl-3-butene-2-ol gave a large yield of acetone and organic nitrate. Acetone may contribute to photolytic OH and HO_2 radicals, and PAN formation in the upper troposphere. Formation of organic nitrate, its yield of the same magnitude as acetone, may also play a significant role in the chemistry of reactive nitrogen in the atmosphere since it can act as a reservoir for NOx. This reservoir may act as a source of NOx and thus enhance the ozone formation in areas remote from the original source of NOx.

Some of the methyl butenols products showed formation of particles. Further investigation of a particle yield event indicated that the observed particle formation had a connection to second-generation products as the reaction proceeded. To understand chemical constituents of particles, an impactor and Teflon filters were employed together with GC-MS and LC-MS for analyses. Neither techniques revealed exact structures of the substance in the condensed phase; however, some evidence indicated multifunctional compounds, which may contain hydroxy, nitrooxy, and/or carbonyl groups, as candidates for particle constituents.

Vapor pressures for some C_3 and C_4, hydroxynitrates were determined to understand the possible contribution to particle formation. Determined vapor pressures were not low enough to form new particles via nucleation or to condense on existing particles.

KYEWORDS: Atmospheric chemistry, troposphere, nitrate radical, unsaturated alcohol, aldehyde, hydroxy alkylnitrate, kinetic, mechanism, aerosol, vapor pressure.

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Enclosed Papers

The thesis is based on the work presented in the following papers:

Paper I **Products from the Gas-phase Reaction of Some Unsaturated Alcohols with Nitrate Radicals**
J. Noda, M. Hallquist, S. Langer, and E. Ljungström
Physical Chemistry Chemical Physics, 2000, 2, 2555-2564.

Paper II **Aerosol formation in Connection with NO_3 Oxidation of Unsaturated alcohols**
J. Noda and E. Ljungström
Atmospheric Environment, 2002, 36, 521-525.

Paper III **Kinetics of Gas-Phase Reaction of Some Unsaturated Alcohols with the Nitrate Radical**
J. Noda, G. Nyman, and S. Langer
Journal of Physical Chemistry A, 2002, 106, 945-951.

Paper IV **Kinetic of the Gas-Phase Reaction of n-C_6–C_{10} Aldehydes with the Nitrate Radicals**
J. Noda, C. Holm, G. Nyman, S. Langer, and E. Ljungström
Submitted to *International Journal of Chemical Kinetics*.

Paper V **On the Atmospheric Fate of C_3 and C_4 Hydroxy Alkylnitrates at Night**
J. Noda, E. Ljungström, K. Treves, and Y. Rudich
Manuscript for *Atmospheric Environment*.