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Visible Light Absorption by Esters and Formation of Organic Acids in the Atmosphere

Aerosols are atmospheric particles that have influence in visibility, climate, and environment. Reports indicate that sulfuric acid is essential for the formation of some aerosol particles and the presence of organic acids enhances the rate of particle formation. The origin of organic acids in the atmosphere is not known and it has been subject to speculation. Some researchers have indicated that organic acids are formed in the atmosphere when reactions occur between volatile organic compounds and free radicals in the upper atmosphere.

The characteristic flavors and fragrances of flowers and fruits are in many cases due to compounds with the ester functional group. Esters are also used in the manufacturing industry as flavoring agents, solvents, and perfumes. Our hypothesis for this proposal is that some organic acids are formed by decomposition of esters that absorb visible radiation as soon as they are released in the lower atmosphere (below 50 km).

We have a research program focused on vibrational fundamental and overtone spectroscopy, as well as atmospheric chemical reactions induced by visible sunlight. The chemical reactions in our studies have activation energies around 200 kJ/mol and could be initiated with visible radiation of a dye laser (wavelength 550-650 nm). These energies are of the same magnitude as the energies of high C-H vibrational overtone transitions (levels with v = 6 or 7). The spectroscopic techniques that are used in our laboratory include cavity ring down at low temperatures to simulate atmospheric conditions and acoustic spectroscopy. Chemical reactions are induced placing a static cell with the sample inside the cavity of a dye laser. For analysis of laser reaction products we use infrared absorption, chromatography, and mass spectrometry. Theoretical simulations of chemical reactions will be done using the Gaussian 03 system of programs. Structures for reactants, products, and transition states will be optimized with several basis sets at different levels of theory (MP3, B3LYP). Thermodynamic quantities such as zero point vibrational energies, temperature corrections, and absolute entropies will be obatined after frequency calculations. First order rate constants will be calculated using the transition state theory.