Geophysical Research Abstracts, Vol. 9, 01828, 2007
SRef-ID: 1607-7962/gra/EGU2007-A-01828

In situ production of HULIS in atmospheric aerosol from the solar photolysis of small molecular weight dicarbonyls

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Colored biogenic polymers are widespread in soils and natural waters. Related but chemically dissimilar organic polymers are also found in the atmospheric aerosol. These polymers, collectively labeled humic-like substances, are known to undergo solar photodegradation into smaller photoreactive species such as α-dicarbonyls. We recently found that the photolysis of the widespread α-dicarbonyl pyruvic acid in water at concentrations commensurate to those in the aerosol proceeds in the opposite direction yielding polyfunctional polymers. This observation implies that the chemical nature and concentration levels of airborne humic-like substances could be the result of *in situ* dynamic photochemical processing. Confirmation of the hypothesis that significant chromophoric species are photochemically polymerized in the condensed phase should have a major impact on our understanding of atmospheric aerosol chemistry and properties. In order to explore the implications of our novel laboratory results on aerosol chemistry, we are determining the chemical structure and the optical and toxicological properties of the polyfunctional polymers produced by ultraviolet irradiation of aqueous solutions of representative α-dicarbonylic and oxocarboxylic species in the presence or absence of ammonium sulfate haze aerosol. Chemical identification is accomplished via electrospray ionization/high-resolution mass spectrometry and one- and two-dimensional ^{13}C- and ^{15}N-NMR spectrometries, complemented with isotopic labeling. Mechanistic studies involve (photo)chemical kinetic and free radical scavenger techniques. Based on our preliminary results, *in situ* photopolymerization of simple carbonyls provides general mechanism for the production of high-molecular mass species in atmospheric aerosol. We have found photo-produced polymers of pyruvic acid (initial MW = 88 amu) with molecular weights as high at 1400

amu with mass median molecular weights of 450 amu.