



Aqueous-phase reactions of oxalic acid with ozone in the presence of pyruvic acid as a photosensitizer

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Aqueous-phase photo-oxidation is an important source of secondary organic aerosols (SOA). SOA material is formed by the mass transfer of low vapor pressure products of the aqueous phase photo-oxidation of soluble VOCs to the aerosol phase. Dicarboxylic acids are ubiquitous in aerosols and they can scatter solar radiation similar to sulfate aerosols. Therefore, these aerosols do not have a direct aerosol heating potential, but a cooling effect on the climate. Among them, pyruvic acid differs being a keto acid, with its $\pi^* \leftarrow n$ electron transition of the keto group around 325 nm.

In this study we concentrated on a more complex system which is actually very typical for atmospheric aqueous phase. Hence, for the first time worldwide we studied the role of pyruvic acid as photosensitizer in the reactivity of ozone toward organic acids (such as oxalic, which is the most abundant diacid in the atmospheric aqueous and particulate phase) and tried to identify the aqueous phase products.

Aqueous-phase reactions were conducted in a rotary evaporator thermostated at 25°C. Solutions of pyruvic acid, oxalic acid or mixture of both were exposed to 360 ± 20 ppb of ozone in synthetic air and/or to UV/VIS light for time period of 2 to 12 hours. A Xe lamp placed at 5 - 10 cm from the reactor was chosen as a light source. All samples were analyzed by high performance liquid chromatography (HPLC). In addition, reaction products were analyzed by mass spectrometer equipped with electrospray ionization source (ESI-MS).

In the presence of ozone only, almost no changes were observed in the samples compo-

sition. After light irradiation only, new broad peaks appeared at longer retention times. Similar behavior was observed when ozone was additionally introduced into the reaction chamber. Our work strongly demonstrates the formation of organic fractions with higher molecular masses, which most probably are formed through oligomerization.