



Investigation of the oxidation mechanisms of limonene photosensitized by imidazole-2-carboxaldehyde

Stéphanie Rossignol, Liselotte Tinel, Kifle Aregahegn, and Christian George

Université de Lyon, Université Lyon 1, CNRS, UMR5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, Villeurbanne, F-69626, France

Recent studies have revealed the significant formation of light absorbing materials, including imidazole and imidazole derivatives, in aqueous aerosol mimics in the presence of both ammonium sulphate and glyoxal (Galloway et al. 2009; Yu et al. 2011; Kampf et al. 2012). Besides the potential impact on radiative properties of secondary organic aerosols, our team has shown that imidazole-2-carboxaldehyde (IC) acts as a photosensitizer, initiating aerosols growth in the presence of gaseous limonene and UV/visible light (Aregahegn et al., abstract submitted).

This work focuses on the characterisation of the chemical mechanisms leading to this aerosols growth, and on the major products identification. The molecular composition of organic/aqueous solutions exposed to UV/visible light and containing IC and limonene is followed in time by HR-ESI-MS/MS in positive and negative modes. Limonene consumption is followed by HPLC-UV. HR-ESI-MS/MS analyses are performed in parallel on IC/ammonium sulphate aerosols exposed to gaseous limonene and UV/visible light, in particular to assess the relevance of in solution experiments. Besides, the lifetime of the triplet state of IC in aqueous/organic solutions in the presence of different terpenes is monitored by laser photolysis experiments and compared in order to explain the first steps of the photosensitized reaction.

First HR-ESI-MS/MS results show the formation of the major "traditional" limonene oxidation products (e.g., coming from gas phase limonene ozonolysis) during the irradiation of organic solutions containing IC and limonene: limononaldehyde, keto-limononaldehyde, limonic acid, limononic acid ... Hundreds of other oxygenated species are however detected, typically with a number of carbon atoms ranging from 4 to 20 and with O/C ratios ranging from 0.2 to 0.7. Monomers and dimers of limonene oxidation products are observed but species with lower carbon numbers than monomeric compounds are predominant. Moreover, and surprisingly, the production rates of all products tend to increase with reaction time and the limonene consumption presents an apparent linearity. These preliminary findings would suggest, in our experimental conditions, an oxidation mechanism initiated by a relatively slow photosensitized process e.g., electron transfer from limonene to the triplet state of IC (which formation is confirmed by laser photolysis experiments), followed by an increase of radicals in the solution leading to an extended limonene oxidation. The UV radiation, and/or the low concentration of reactants, are susceptible in our context to limit the formation of oligomers (Bateman et al. 2011) and promote fragmentation pathways. If these hypothesis need to be confirmed, this study appears to be a pertinent way to investigate the mechanisms and to assess the importance of photosensitized reactions in secondary organic aerosols growth and, possibly, in other air/condensed phase surfaces present in the environment, such as air/sea interface.

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