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Photooxidation of dicarboxylic acids—Part I: Effects of inorganic ions on degradation of azelaic acid

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Abstract

In this paper, the first of a two-part series, effects of chloride, sulfate, and nitrate ions and pH on photooxidation of azelaic acid were investigated in an aqueous system. Nitrate ions play the major role in accelerating photooxidation of azelaic acid by increasing •OH concentration, while chloride ions consume •OH concentration and retard photooxidation rates. In inorganic mixtures, a nitrate-to-chloride molar ratio of >1.5 accelerated photooxidation of azelaic acid indicating the dominant role of nitrate. Substantial inhibition effects of chloride on photooxidation of azelaic acid were demonstrated at a nitrate-to-chloride molar ratio <0.3. Nitrate and chloride are interrelated in affecting photooxidation of azelaic acid as photolysis of nitrate would significantly consume H^+, retarding reaction of $HOCl^-$ with H^+, and consequently decreasing •OH-chloride reaction. pH affects photooxidation of C_2–C_9 dicarboxylic acids (DCAs) in two ways: C_2–C_4 dicarboxylates exhibit substantially higher degradation rates than their parent DCAs, while C_5–C_9 dicarboxylates demonstrate degradation rates similar to their parent DCAs.

Keywords: Dicarboxylic acid; Azelaic acid; Photooxidation; Inorganic species; Ionic strength

1. Introduction

Low molecular weight (LMW) C_2–C_9 dicarboxylic acids (DCAs) in aerosols have received increasing attention in recent years because of their potential of altering hygroscopic properties of aerosols as cloud condensation nuclei (Cruz and Pandis, 1997). Most researchers have mainly focused on identifying airborne DCAs in atmospheric aerosols (Kawamura and Ikushima, 1993; Kerminen et al., 1999; Limbeck et al., 2001; Yao et al., 2004; Yue and Fraser, 2004), and have found DCAs in wet deposition (Sempéré and Kawamura, 1996; Kawamura et al., 2001) and cloud water (Hegg et al., 2002; Marinoni et al., 2004). Although ambient C_2–C_9 DCAs appeared to be closely associated with in-cloud processes (Yao et al., 2002; Mochida et al., 2003; Lee et al., 2002, 2003), and could be formed and degraded in cloud droplets through initial attack of hydroxyl radicals (•OH) (Ervens et al., 2004), enhanced understanding is needed regarding their photooxidation mechanisms

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and effects of abundant atmospheric inorganic ions on their atmospheric reactions.

Nepotchatykh and Ariya (2002) have examined ozone oxidation of C_2–C_9 DCAs in an aqueous environment, and suggested that •OH, rather than ozone, is the major oxidant of DCA photodegradation in atmosphere. While a few field observations suggest that longer-chain DCAs can be precursors of smaller DCAs in atmosphere (Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999; Yu et al., 2005), experimental evidence is needed to verify potential reaction pathways. To address these issues, we have investigated photooxidation of ambient DCAs relevant in atmospheric aqueous environments (e.g., cloud and fog droplets) in a two-part study. In this first part of the study, we present the effects of pH, ionic strength, and abundant inorganic species (chloride, sulfate, and nitrate) on •OH-DCA oxidation rates. Three major inorganic species, Cl^-, NO_3^- and SO_4^{2-}, were selected because they are closely associated with sea-salt, wind-blown dust, and anthropogenic emissions. In addition to individual effects of each inorganic species, combined effects of chloride, sulfate and nitrate mixtures were examined on concentrations of •OH in the reaction system and oxidation rates of azelaic acid. Azelaic acid was selected as the model compound because it can exhibit high concentrations, e.g., at least 1.4 times higher than DCAs containing more than five carbons in marine and urban atmospheric particulates (Kawamura and Gagosian, 1987; Kawamura and Ikushima, 1993). In addition, investigation of photodegradation of azelaic acid is advantageous to observe relevant intermediates (e.g., smaller DCAs) in the atmosphere.

The second paper in this study examines photooxidation kinetics of individual C_2–C_9 DCAs and possible reaction mechanisms based on concentration profiles of identified intermediates. Additional insights about ambient DCAs were obtained from comparison of our laboratory studies with relevant field observations.

2. Experimental

2.1. Liquid-phase photooxidation system

We employed a liquid-phase photooxidation system (Fig. 1) consisting of an annular cylindrical reactor with a quartz sleeve at the center of the reactor to house a 16-W UV light source (Ster-L-Ray^{TM}, Atlantic Ultraviolet Corp., USA). Photooxidation was carried out in a semi-batch fashion; i.e., 150 mL of solution (in ultrapure DI water) was circulated at a flow rate of 150 mL min^{-1}, with a residence time outside of the reactor for around 30 s. Depending on degradation rates under various reaction conditions, 0.5 mL aliquot was sampled every 15–45 min. Total volume of the withdrawn samples was $<5\%$ of the solution. Each aliquot sample was further diluted to 1.0 mL for following chemical analyses.

The UV light source provided a principal output at 254 nm (≈ 13 mW cm^{-2}) and a small amount of radiation at 185 nm (<1.0 mW cm^{-2}), which induced formation of ozone from dissolved oxygen followed by generation of H_2O_2. In turn, H_2O_2 underwent photolysis (under 254 nm) and was one of •OH sources in the reaction system. The radiation of 185 nm was mostly absorbed by water to subsequently produce •OH, which also minimized photolysis of other compounds during reactions in this study. Our laboratory tests showed that C_2–C_9 DCAs have negligible absorbance at 254 nm, and exhibited minimal photolysis. In addition, the

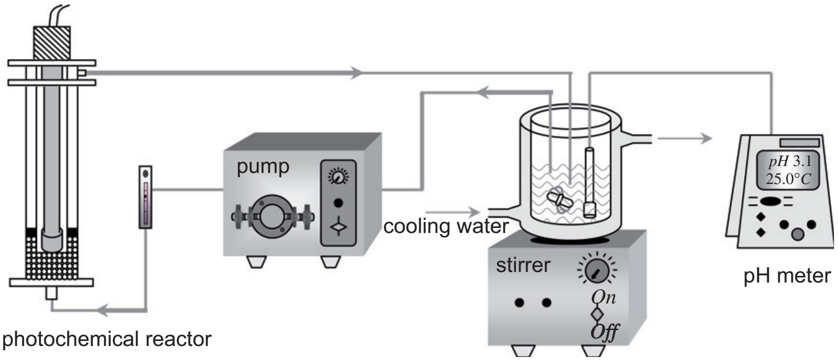

Fig. 1. Schematic setup of liquid-phase photochemical reaction system.