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学 位 論 文 題 名

Identification of hydroxy and keto-dicarboxylic acids in remote marine aerosols: Implications for photochemical formation and transformation of water-soluble organic aerosols
（外洋エアロゾル中のヒドロキシおよびケトジカルボン酸の同定：水溶性有機エアロゾルの光化学的生成と変質への関係）

Understanding the composition of atmospheric organic particulate matter is essential for predicting its effects on climate, air quality, and health. Dicarboxylic acids (diacids) are dominant components of organic aerosols in the atmosphere and have been extensively studied at many locations around the world. Because of their high water solubility and hygroscopic properties, particles enriched with diacids play an important role as cloud condensation nuclei (CCN) and ice nuclei (IN) affecting the radiative forcing of the Earth. In spite of their ubiquity in the Environment and their high reactivity, there are some diacids related compounds containing hydroxyl and keto groups that have been suggested to exist in the atmosphere but have never been identified in marine aerosols. Due to the enhanced polarity compared with diacids, these compounds should play a crucial role as CCN and IN. Identification of these compounds is important to a better understanding of the photochemical process and chemical composition of organic particulate matter, as this chemical composition is essential for predicting the effects on climate, air quality, and human health. In the present study, the author focused on identification, quantification, seasonal distribution and formation pathways of atmospherically important hydroxy and keto-diacids. The first chapter of this thesis is general introduction to diacids and related compounds, their significances in the atmosphere with recent scientific updates.

The second chapter of this thesis will focus on identification of hydroxy and keto-dicarboxylic acids in remote marine aerosol samples. Remote marine aerosols collected at Chichijima Island were studied for hydroxy and keto-diacids. A two-step derivatization technique was employed, using 14% BF_3/n-butanol for the butylation of carboxyl groups and acidic ketones followed by N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) for the trimethylsilylation of hydroxyl groups. Several new peaks were detected in the gas chromatogram after trimethylsilylation of the dibutyl ester fraction. Based on mass spectral interpretation with authentic standards, the author successfully identified and quantified a homologous series of hydroxydiacids (hC_3–hC_6), includes tartronic acid, malic acid, 3-hydroxyglutaric acid, 2-hydroxyglutaric acid, 2-hydroxyadipic acid, 3-hydroxyadipic acid, and tartaric acid. Ketodiacids includes oxaloacetic acid (kC_4).

The third chapter of this thesis focused on seasonal variations of hydroxy and keto-diacids at Chichijima Island, shows maximum in spring followed by winter and autumn. Molecular compositions of hydroxy and keto-diacids show predominance of malic acid followed by tartronic acid. Total hydroxy and keto-diacids maximized in spring when air masses originated from the Asian Continent with westerly winds. Significant positive correlation was observed between hydroxydiacids and diacids compounds in all four seasons suggest that hydroxydiacids and diacids have similar sources. This study demonstrates that the ambient aerosols at Chichijima Island are strongly influenced by long-range atmospheric pollutants from East Asia in winter/spring and by photo-oxidation process they are converting into low molecular weight diacids through intermediates.

The fourth chapter describes about photochemical processing of hydroxy and keto-diacids, the author conducted batch UV irradiation experiments on two types of samples collected from India, which symbolize anthropogenic (AA) and biogenic aerosols (BA), for time periods of 0.5 to 120 h. The results show that photochemical degradation of tartronic (hC_3), malic (hC_4), 2-hydroxyglutaric (2-hC_5), and 2-hydroxyadipic acids (2-hC_6) and keto form of oxaloacetic acid overcome their production in aqueous aerosols. Whereas, 3-hydroxyglutaric acid (3-hC_5), tartaric acid, 3-hydroxyadipic acid (3-hC_6), enol form of oxaloacetic acid showed a significant increase during the course of irradiation experiment upto some extent then decrease. And also found a gradual decrease in the relative abundance of hC_4 to total hydroxy diacids and an increase in the relative abundance of enol form of oxaloacetic acid during prolonged experiment. Based on the changes in concentrations and mass ratios of selected species with the irradiation time, the author suggests that hydroxydiacids are the key intermediates in the degradation of smaller diacids. This study demonstrates that the ambient aerosols contain abundant precursors that produce diacids via intermediates such as hydroxy and keto-diacids.

In the fifth chapter the author describes about aqueous phase photooxidation of anthropogenic (toluene, Benzene) and biogenic precursors (isoprene and α-pinene) via laboratory experiments. The preliminary results of this study suggest the production of diacids and related compounds in aqueous phase by the photooxidation of anthropogenic and biogenic precursors are significant.

In addition to the excellent academic knowledge in the research, her academic records throughout the Ph. D course are excellent. Based on these evidences, the committee reached to a conclusion that Divyavani deserves to become a Doctor of Environmental Science.