

Chapter 1

Introduction

The study of the chemical effects resulting from the irradiation of ice/snow field samples or laboratory-produced frozen aqueous solutions with UV light is a relatively new and active research area relevant to atmospheric chemical processes taking place in high latitude environments. A variety of photochemical reactions involving inorganic¹⁻¹² and organic¹³⁻²¹ ice dopants has been studied. Ultraviolet light is effective at promoting photochemical and post-irradiation reactions in ice. However, there are difficulties controlling the production of ice and snow samples in the laboratory. In addition, there are few techniques for real-time reaction monitoring in the ice matrices.

Ice photochemical processes may provide an explanation for the observed excess of carbonyl oxides found in some Greenland ice cores over the last millennium relative to contemporaneous Antarctic ice core records.²² Photolysis of the organic compounds accumulated in snow appears to have an impact on the composition of the lower atmosphere in early polar spring.^{3,23} In addition, the photochemical transformation of organic compounds trapped in snow and ice may produce more persistent, bioaccumulative, and potentially toxic chemical species.¹⁷

The principal research objective of this thesis was to investigate the kinetics, mechanism, and photo-efficiencies of the photochemical decomposition of pyruvic acid, an α -ketocarboxylic species, which is present in polar ice.²⁴ In order to improve our understanding of the photochemical fate of pyruvic acid in water and ice, several different experimental approaches were taken as described in the subsequent chapters.

In Chapter 2, the conceptual framework to the chemistry involved in the photooxidation and photodecomposition of ketocarboxylic ice core dopants is presented.

This is followed by a discussion of the relevance of this photochemistry to historical CO and CO₂ ice core records.

In Chapter 3, the functional state of the photoreactive carbonyl-form of pyruvic acid is examined. The reversible hydration of pyruvic acid that occurs in quasi-liquid layers of ice was studied using solid-state magic-angle-spinning nuclear magnetic resonance in deuterated water and ice.²⁵

In Chapter 4, the photochemical rates and products of reaction at room temperature are determined as a function of reactant concentrations, and scavenger effects, quantum yields for the photoinduced oligomerization of aqueous pyruvic acid, which are also applicable to the conditions found in haze aerosol, are measured. In order to unravel mechanistic details, the photoreaction was followed by liquid chromatography with UV detection and ESI-MS. These detection methods were complemented by collisional induced dissociation, ²H- and ¹³C-isotope labeling experiments, and ¹³C-NMR measurements.²⁶

In Chapter 5, we establish that the intermediate species which participate in the primary photoprocess in ice are distant triplet radical pairs. The experimental results are consistent with *n-π** excitation of pyruvic acid, which induces long-range electron transfer from the excited carbonyl chromophore to neighboring carbonyl acceptors.²⁰

In Chapter 6, the kinetics of photolysis of frozen aqueous pyruvic acid samples are determined. The release of photochemical reaction products to the gas phase is monitored in real time. The photochemistry of pyruvic acid in the frozen state is compared to the same process in the liquid phase. A comprehensive reaction mechanism is proposed.²¹

In Chapter 7, we improve an existing model of photochemistry of dissolved organic matter in glacial ice. We estimate the contribution of this mechanism to CO and CO₂ production in glacial ice.

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