

# Ultraviolet photolysis of amino acids in a 100 K water ice matrix: Application to the outer Solar System bodies

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## Abstract

We report the rates of decomposition by ultraviolet (UV) photolysis of four amino acids in millimeter-thick crystalline water ice matrices at 100 K to constrain the survivability of these important organic molecules within ice lying near the surfaces of outer Solar System bodies. We UV-irradiated crystalline ice samples containing known concentrations of the amino acids glycine, aspartic acid, glutamic acid, and phenylalanine, then we measured the surviving concentrations using high performance liquid chromatography (HPLC) with fluorescence detection. From these experiments, we determine photolytic decomposition rates and half-lives. The half-life varies linearly with the ice thickness for all acids studied here. For example, glycine is the most resistant to photolytic destruction with a half-life of 50, 12, and 3.7 h in 1.6, 0.28, and 0.14 mm thick ices, respectively. We explain this linear variation of half-life with thickness as a consequence of extinction, mostly due to scattering, within these macroscopically thick ice samples. Applied to low latitude surface ice on Jupiter's satellite Europa, this analysis indicates that the concentration of any of these amino acids within the top meter of similar ice will be halved within a  $\sim 10$  year timescale.

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## 1. Introduction

Water ice is present throughout the outer Solar System and appears in a crystalline phase, even when found on bodies where low surface temperatures suggest that the amorphous phase might be favored (Jewitt and Luu, 2004). The photolytic properties of compounds in crystalline ice matrices are important to our understanding of chemical reactions occurring within the surface ices on outer solar bodies. The recent discovery of water vapor plumes ejected from fissures near the south pole of Saturn's satellite Enceladus (Parkinson et al., 2006) suggest that complex organic chemistry may occur even in the extreme environments of the icy satellites of the outer planets. Evidence of organic species and crystalline water ice in the vicinity of the Enceladus "tiger stripes" is reported from Cassini-VIMS spectra (Buratti, 2005; Johnson, 2005). These observations support the need for laboratory studies of pho-

tolysis of organics in cryogenic crystalline water ices that are analogs of outer Solar System ices.

Since the first suggestions of the presence of a subsurface, liquid water ocean on Europa, Europa has become a prime target of astrobiological interest. The likelihood of a subsurface ocean on Europa led to questions of possible endemic organic chemistry within the liquid layer. Europa's low density of impact craters indicates extensive resurfacing (Malin and Pieri, 1986; Greenberg et al., 2003; Figueredo and Greeley, 2004). Organics originating in the subsurface liquid water or "warm ice" may be extruded onto the surface from a liquid water reservoir at depth during resurfacing events associated with the globally distributed linea and "bands," long linear "cracks" in a high albedo ice surface (Malin and Pieri, 1986; Greenberg et al., 2003; Nimmo et al., 2003; Nimmo, 2004), or during activity in the "chaotic terrain" (Goodman et al., 2004). Other potential sources of organic compounds or their components on the surfaces of the jovian moons may include impacts of carbonaceous chondrites that contain amino acids, purines, pyrimidines and polymers, as well as simple organic compounds and hydrogen cyanide from comets (Cronin and

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Chang, 1993; Levy et al., 2000; Huang et al., 2005; Pierazzo and Chyba, 2002). Levy et al. (2000) simulated prebiotic synthetic processes under Europa-like conditions where diluted solutions of  $\text{NH}_4\text{CN}$  were frozen for 5 and 25 years and simple amino acids dominated by glycine formed in the frozen samples.

We chose the experimental conditions in the present study for their relevance to crystalline ices in the outer Solar System in contrast to the ices found in dense protostellar clouds where temperatures are on the order of  $\sim 10$  K and amorphous ices are assembled from gas phase molecular reactions on small grains (Allamandola et al., 1988). Previous experiments on amino acids in analogs of these “astrophysical ices” focused on  $\mu\text{m}$ -thick transparent layers of amorphous ice grown by vapor deposition (Ehrenfreund et al., 2001; Bernstein et al., 2002). Recently, ten Kate et al. (2006) investigated the photolytic destruction of glycine in  $0.3 \mu\text{m}$  thick polycrystalline films at 210 K under martian conditions.

In our experiments, we froze aqueous solutions of amino acids to  $\sim\text{mm}$ -thick samples of crystalline phase hexagonal ice at 100 K. Such ice samples frozen from liquid water and cooled to 100 K have high albedo and appear “white” due to multiple scattering from internal microstructures. The survival of amino acids that exist in thick, strongly scattering, high albedo, cryogenic crystalline ices exposed to UV radiation is the focus of this study. It should be noted that UV radiation is not necessarily the dominant source of radiation on the surface of icy Solar System bodies. For example, Europa’s surface is subject to bombardment by highly energetic electrons and ions that are trapped in the jovian magnetic field with electrons comprising 80% of the total energy flux. Specifically, the energy flux due to these energetic particles is  $5 \times 10^{10} \text{ keV cm}^{-2} \text{ s}^{-1}$  while the UV energy flux is  $<1\%$  of that value (Carlson et al., 1999; Cooper et al., 2001).

High energy particles have more severe effects on organic material; however, they have limited penetration into the ice layer (i.e.  $\sim 1 \mu\text{m}$  for energetic electrons). Although this is also true for short wavelength photons (i.e. Lyman- $\alpha$ ), photon penetration depths rise sharply for wavelengths greater than  $\sim 150 \text{ nm}$ . As will be discussed in Section 4, the penetration depth of photons in crystalline water ice increases from  $1 \mu\text{m}$  at 163 nm to 1 cm at 180 nm and up to a 1 m at  $\sim 200 \text{ nm}$ . Therefore, the effects of UV radiation are highly relevant to the survival of compounds located within the upper meter of an icy surface.

## 2. Experiments

### 2.1. Apparatus

Photolysis experiments were conducted using an in-house designed vacuum chamber whose ultimate pressure is on the order of  $\sim 10^{-5} \text{ Pa}$ . The chamber is equipped with multiple ports whose axes intersect at a common point within the chamber. A close-cycled He cryostat (Advanced Research, Inc., model CSW-202B for UHV applications) or “cold-finger,” in conjunction with a Lakeshore temperature controller (Model 330),

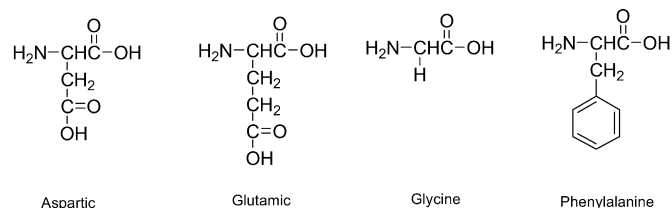


Fig. 1. Structures of amino acids included in the present research.

enabled sample temperatures to be maintained at programmed values down to  $\sim 18 \text{ K}$  ( $\pm <1 \text{ K}$ ) without thermal shielding. The cold finger was mounted so that cryogenic samples were positioned in the chamber with their surface centers at the intersection point of the chamber port axes. Further, the cold-finger was free to rotate under vacuum so the samples could face any one of the port axes.

An Argon mini-arc lamp (National Bureau of Standards; Klose et al., 1987) mounted on one of the chamber ports, provided a continuum and well-calibrated UV light source. The lamp was typically operated with an arc current of 40 A passing through electrodes bathed in a flow of ultra high purity Argon gas. Samples were irradiated through a  $\text{MgF}_2$  window from a distance of 50 cm between the arc center and the sample surface if not stated otherwise. A collimating aperture was placed on the lamp window to allow uniform illumination of the sample surface. The output flux of the lamp was independently calibrated using chemical actinometry with potassium ferrioxalate (Parker, 1953; Hatchard and Parker, 1956). The UV photon flux (130–335 nm) incident on samples in the present experiments was found to be  $2 \times 10^{14} \text{ photons s}^{-1} \text{ cm}^{-2}$ . This corresponds well to the average flux of  $1.2 \times 10^{14} \text{ photons s}^{-1} \text{ cm}^{-2}$  calculated from the lamp’s original calibration data for the 163 to 300 nm wavelength range.

### 2.2. Methodology

Experiments were carried out with crystalline water ice samples containing known concentrations of amino acids. Structures of amino acids included in the present study are shown in Fig. 1. In total, three amino acid standard solutions, and three types of ice samples were prepared (Table 1). Two standard solutions contained single-amino acids; namely D-phenylalanine at  $2.00 \times 10^{-4} \text{ M}$  and D,L-phenylalanine at  $1.64 \times 10^{-4} \text{ M}$ . The third standard solution was a mixture of D,L-aspartic acid (ASP), D,L-glutamic acid (GLU), glycine (GLY) and D,L-phenylalanine (PHE) with individual concentrations of  $1.36 \times 10^{-4} \text{ M}$ ,  $1.64 \times 10^{-4} \text{ M}$ ,  $1.73 \times 10^{-4} \text{ M}$ , and  $1.45 \times 10^{-4} \text{ M}$ , respectively. Amino acids were purchased from Sigma-Aldrich (99% purity or better) and they were used as received. All solutions were prepared with deionized water from a NANOpure Ultrapure water system (Barnstead). The standard amino acid abbreviations, shown in parenthesis above, are used throughout the remainder of the manuscript.

Three different thickness ice samples were measured. The thickest ice samples were prepared by depositing  $300 \mu\text{L}$  of amino acid solution into a cylindrical sample cup of oxygen free high conductivity (OFHC) copper mounted on the end of the

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