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The radiation stability of glycine in solid CO_2 – *In situ* laboratory measurements with applications to Mars

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ABSTRACT

The detection of biologically important, organic molecules on Mars is an important goal that may soon be reached. However, the current small number of organic detections at the martian surface may be due to the harsh UV and radiation conditions there. It seems likely that a successful search will require probing the subsurface of Mars, where penetrating cosmic rays and solar energetic particles dominate the radiation environment, with an influence that weakens with depth. Toward the goal of understanding the survival of organic molecules in cold radiation-rich environments on Mars, we present new kinetics data on the radiolytic destruction of glycine diluted in frozen carbon dioxide. Rate constants were measured *in situ* with infrared spectroscopy, without additional sample manipulation, for irradiations at 25, 50, and 75 K with 0.8-MeV protons. The resulting half-lives for glycine in CO_2-ice are compared to previous results for glycine in H_2O-ice and show that glycine in CO_2-ice is much less stable in a radiation environment, with destruction rate constants ~20–40 times higher than glycine in H_2O-ice. Extrapolation of these results to conditions in the martian subsurface results in half-lives estimated to be less than 100–200 Myr even at depths of a few meters.

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1. Introduction

Many planetary bodies of astrobiological interest, such as Mars, are exposed to harsh incident radiation, which will influence the times that molecules can survive on them. Some or all of these bodies may well contain biologically-important organic molecules, some may even have supported life at some point in their history, and some may support life today. However, in the case of Mars, the Viking instruments were designed to search for evidence of life on the martian surface (e.g., Anderson et al., 1972), but no organics were definitively detected (although a reanalysis suggests organic molecules may have been overlooked; see Navarro-Gonzalez et al., 2010). Recently, chlorinated benzene was identified by the SAM instrument on the Curiosity Rover in samples drilled from rocks in Yellowknife Bay on Mars (Glavin et al., 2015), a sign that organic molecules may indeed survive just beneath the surface there. During flybys of Europa, near-infrared spectra from the Galileo-NIMS instrument showed no clear indications of organic molecules in surface ices (Carlson et al., 2009), although these remote observations had significant inherent limitations due to the harsh radiation environment around Jupiter. Despite the recent upturn of results for one of these bodies, the history of non-detections for the surfaces of Mars and Europa are surprising because even if there is no endogenous organic material present, one expects a significant number of exogenous molecules delivered by meteorites, comets, and interplanetary dust particles. For example, it has long been known that amino acids are present in the organic components of carbonaceous meteorites such as Murchison (Cronin et al., 1979), and more recently, organics have been detected in the tracks of cometary dust particles collected by the Stardust spacecraft as it flew through the coma of Comet 81P/Wild 2. See Sandford et al. (2006) – one reason for the lack of organics found on both Europa and Mars is radiation-driven molecular destruction. Successful searches for organic molecules on these worlds likely will require sampling their subsurfaces, where organics may be frozen in ices dominated by either H_2O or CO_2, which provide some protection from ionizing radiation. On Mars, solid CO_2 is observed in polar regions during martian winter, and may persist throughout the summer in the southern polar region beneath the surface (Malin et al., 2001; Phillips et al., 2011), where organics and H_2O also are likely to be embedded. Subsurface H_2O-ice on Mars may exist at various depths and experience seasonal temperature variations from 150 to 200 K (see, for example, thermal modeling by Bandfield, 2007). Turning to Europa, its surface consists of an H_2O-dominated ice shell at a temperature of

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~100–130 K (Carlson et al., 2009), whose chemistry is driven primarily by the bombardment by magnetospheric charged particles (keV-MeV electrons, especially in the trailing hemisphere; Paranicas et al., 2009).

The radiation doses received by molecules on planetary bodies depend on many factors and are extremely sensitive to depth beneath an exposed surface. For Mars, UV photons dominate at the near-surface (depths less than a few μm), whereas galactic cosmic rays and solar energetic particles (mainly protons) dominate the subsurface particle-radiation environment. The MSL-RAD instrument recently measured the surface dose rate to be about 0.08 Gy yr^{-1} (Hassler et al., 2014), which is estimated to decrease with depth according to the content of the overlying material by factors of 5–10 to a depth of a few meters (also see Dartnell et al., 2007).

To accurately simulate and predict radiation-chemical behavior of organic molecules on Mars and other planetary bodies, kinetics data at large dilutions must be measured or extrapolated from existing data since accurate *a priori*, *ab initio* calculations are not feasible. Factors such as reactions of the surrounding material, for example an ice, or its radiation-chemical products are important and can be studied through reaction kinetics. Along these lines, in previous studies by our group we measured the radiation-chemical kinetics of glycine, the simplest amino acid, in H_2O-dominated ice mixtures relevant to icy planetary environments, with a focus on glycine's survival in the martian subsurface (Gerakines et al., 2012; Gerakines and Hudson, 2013). An important observation was that rate constants and half-lives for the radiolytic destruction of glycine depend both on temperature and glycine concentration in H_2O-ice.

Outside of our own results, reports of the radiolytic decay of glycine are either based on analyses performed at room temperature or with glycine in an undiluted crystalline form. Moreover, most experiments in the literature were not performed at temperatures or with compositions appropriate to the surface of Mars or other Solar System bodies, and the irradiated glycine samples were measured after significant sample handling and possible chemical alteration. For example, a commonly cited result is that of Kminek and Bada (2006), who gamma-irradiated dry glycine powder in sealed vials. After irradiation, the vials were opened and the contents dissolved in water for room-temperature liquid-chromatographic analysis to determine the loss of glycine, clearly compromising the details of the irradiation chemistry. Pilling et al. (2013) used infrared spectroscopy to measure the destruction rates of glycine polymorphs after exposure to 1-MeV protons, with most measurements again being made at room temperature. The α crystalline form of glycine was found to be the more susceptible to radiation-induced destruction, with the β form being destroyed five times slower. These results agree with our own work (Gerakines et al., 2012).

Low-temperature (~10–30 K) glycine destruction also has been studied by other groups, some using *in-situ* methods. Pernet et al. (2013) used near-edge X-ray absorption spectroscopy to study the X-ray induced destruction rates of glycine in the absence and presence of H_2O-ice at 30 K. They concluded that dilution in H_2O-ice did not affect glycine's destruction rate, and predicted glycine half-lives of about 1 year at 1 AU from the Sun. However, their measurements of radiation dose were restricted to the exposure time for each sample and no measurements of *absorbed* radiation doses could be made, making half-life comparisons for wet and dry samples difficult. Johnson et al. (2012) measured glycine destruction at 18 K in an argon matrix (Ar:gly ratio ~10,000:1) exposed to UV photons from three sources with different emission lines. Results showed that glycine was easily destroyed by UV photons, such as would be present at the surface of Mars or Europa, with half-lives of a few years. Orzechowska et al. (2007) also used UV photolysis to measure the photo-destruction of glycine, but in mm-thick H_2O-ice samples at 100 K. Their analyses used room-temperature liquid chromatography, again requiring the melting of the ice samples after photolysis. Even earlier work is available on the photo-destruction of amino acids at 12 K, for applications to interstellar chemistry, but there too only incident fluences (photons cm^{-2}) were measured, not absorbed energies (Ehrenfreund et al., 2001).

In short, we know of no published *in-situ* determinations of low-temperature radiolytic destruction of glycine or any other amino acids mixed with H_2O-ice other than our earlier work (Gerakines et al., 2012; Gerakines and Hudson, 2013). For the case of amino acids, such as glycine, in CO_2-ice the literature is even sparser. Although CO_2 is a major constituent of ices on cold planetary bodies, no radiation-chemical results for mixtures of CO_2 + glycine are in the literature. Therefore, in the present study we report laboratory measurements of the survival of glycine diluted in CO_2-ice at several concentrations (CO_2:glycine = 75:1, 150:1, 190:1, 250:1, and 380:1) and at three temperatures (25, 50, and 75 K). For each sample, we measured the destruction yield (*G*-value), destruction rate constant, and half-life dose of glycine due to irradiation by 0.8-MeV protons. All measurements were made *in situ* at the temperature of irradiation using infrared (IR) spectroscopy. While the temperatures and concentrations were limited by experimental constraints and do not mimic those on Mars or Europa, observed trends in the laboratory results can be extrapolated to relevant planetary environments.

2. Experimental details

2.1. Sample preparation

The experimental system in the Cosmic Ice Laboratory at the NASA Goddard Space Flight Center has been described in detail (Hudson and Moore, 1999), and the details of the most current set-up can be found in our previous study on amino acids (Gerakines et al., 2012). In summary, our system consists of a high-vacuum chamber ($P = 5 \times 10^{-7}$ torr at 300 K) mated to the beam line of a Van de Graaff accelerator and to an IR spectrometer (Nicolet Nexus 670 FT-IR). A polished aluminum substrate (area ≈5 cm^2) is mounted inside the chamber on the end of the cold finger of a closed-cycle helium cryostat (Air Products Displex DE-204) capable of cooling to a minimum of ~15 K. The substrate's temperature is monitored by a silicon diode sensor and can be adjusted up to 300 K using a heater located at the top of the substrate holder. This same substrate is positioned so that the IR spectrometer's beam is reflected from the substrate's surface at a near-normal angle (~5°) and directed onto an HgCdTe (MCT) detector. With an ice sample on the metal substrate, the IR beam passes through the sample before and after reflection off the underlying metal surface. The substrate is fully rotatable through 360° to face the IR spectrometer, the Van de Graaff accelerator, and other components.

Samples were prepared as follows. A custom-built Knudsen-type sublimation oven, attached to one port of the vacuum chamber, was used to sublime glycine into the chamber and produce micrometer-thick films on the cold substrate (for more details about the oven see Gerakines et al., 2012). With about 50 mg of glycine in the sublimation oven, it was heated (to 160 °C) until a sufficient amount of glycine vapor was produced to create a sample. At that point, CO_2 vapor was released into the vacuum chamber in front of the oven using a metered leak valve, which was calibrated as described by Gerakines et al. (2012) to achieve the desired CO_2-to-glycine ratio for the sample to be studied. With both gases flowing, the cold (25 K) substrate then was rotated to face the oven, and the sample's growth was measured by monitoring the interference fringes of a 650-nm laser beam reflected from