Synthesis of Prebiotic Glycerol in Interstellar Ices**

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Materials and Methods

The experimental setup has been described in detail elsewhere.\[^{[1]}\] Briefly, the simulation experiments were conducted in a contamination-free ultra-high vacuum (UHV) chamber at base pressures of a few $10^{-11}$ torr.\[^{[1a]}\] Four sets of methanol ices were prepared on a 6 K target through deposition of the gaseous precursors: CH$_3$OH, CD$_3$OD, $^{13}$CH$_3$OH, and CH$_3^{18}$OH. The 510 ± 10 nm thick ices were irradiated with energetic electrons (5 keV) for one hour at 30 ± 5 nA by scanning the electron beam over an area of 1.0 ± 0.1 cm$^2$ thus exposing the samples to 6.5 ± 0.8 eV per molecule on average and mimicking typical life times of cold molecular clouds of a few $10^6$ years. The choice of low temperature target represents typical temperatures of ice-coated grains in cold molecular clouds; the pressure conditions of a few $10^{-11}$ torr guarantee that over the time scale of each experiment of 15 hours, less than one monolayer of residual gases condensed on the icy target. For the \textit{in situ} identification of new bands emerging, a Fourier Transform Infrared (FTIR) spectrometer (Nicolet 6700) monitored the samples during the irradiation. After the irradiation, temperature programed desorption (TPD) studies were conducted by heating the irradiated ices at a rate of 0.5 K min$^{-1}$ to 300 K. Throughout the sublimation process, the ice samples were monitored via infrared spectroscopy; individual molecules subliming into the gas phase were identified by ionizing the molecules via single photon ionization (PI) exploiting pulsed (30 Hz) coherent vacuum ultraviolet (VUV) light at 118.2 nm (10.49 eV) generated via non-linear four wave mixing; the ions were then extracted into a reflectron time-of-flight (ReTOF) mass spectrometer, whereupon the ions were mass resolved according to their arrival times.\[^{[1b]}\]

Finally, we would like to discuss the source of ionizing radiation (energetic electrons). The experiments are aimed to simulate the interaction of interstellar model ices with galactic cosmic rays (GCRs) to form astrobiologically important molecules. It is very important to highlight that no laboratory experiment can simulate the interaction of the energetic GCRs with ices directly since no experimental device is accessible to the community that can generate a broad range of kinetic energies of protons and helium nuclei – the main constituents of the GCR - from the MeV to the PeV range. However, the physical effects of GCRs interacting with ices are well understood: GCR lose energy predominantly via ionization of the target molecules; the secondary electrons generated can induce further ionization thus creating electron cascades.\[^{[2]}\] By convolving over the energies of the GCR particles, it is feasible to derive a kinetic energy distribution of the electrons generated that are typically in ranges of a few eV up to the 10 keV range. Therefore, rather than exposing the samples to GCR particles, we simulate the GCR processing and irradiate the samples with electrons, here at 5 keV. Their linear energy transfer (LET) is similar to LETs of 10 to 20 MeV GCR protons penetrating ices. The energy transfer from the electrons to the methanol ices was simulated utilizing the CASINO code\[^{[3]}\] yielding an average dose of 6.5 ± 0.8 eV per molecule. Each second in the laboratory simulates the exposure of about $10^{10}$ s in space. Therefore, the complete experiment mimics the exposure of the ices of about $10^6$ years, i.e. typical life times of cold molecular clouds. We acknowledge that we cannot quantify to what extent the glycerol was formed in our experiments during the irradiation and/or in the course of the annealing period via radical recombination; consequently, the experiments presented here do not exactly replicate real interstellar ices. Our ice samples are chosen as predominantly model ices, so that we could demonstrate the proof of concept that glycerol can be formed from these ices upon interaction with ionizing radiation.
Figure S1: Reflectron time-of-flight (ReTOF) mass spectra as a function of temperature of the newly formed products subliming into the gas phase from radiation processed isotopically labelled methanol ices obtained at photoionization energy of 10.49 eV.
Figure S2. Infrared spectra of liquid (a) ethylene glycol and (b) glycerol taken from the NIST database.
Figure S3. Sublimation profiles of the methanol molecules (CH$_3$OH, CD$_3$OD, CH$_3^{18}$OH, $^{13}$CH$_3$OH) obtained from a residual gas analyzer at an electron impact energy of 100 eV (left) and sublimation profiles of ethylene glycol isotopomers (HOCH$_2$CH$_2$OH, DOCD$_2$CD$_2$OD, H$_2$OCH$_2$CH$_2^{18}$OH and HO$^{13}$CH$_2$$^{13}$CH$_2$OH) extracted from ReTOF data obtained after photoionization with 10.49 eV from the irradiated methanol isotopologues ices. The ionization energy of methanol (10.84 eV) is above 10.49 eV. Consequently the sublimation profile was recorded with a standard quadrupole mass spectrometer using electron impact ionization of the neutral molecules.
Figure S4. Infrared spectra were also recorded during the temperature programmed desorption at (c) 160 K after the methanol and (d) at 210 K after the ethylene glycol sublimation.

