Reaction Mechanism

DOI: 10.1002/ange.201408729

Synthesis of Prebiotic Glycerol in Interstellar Ices**

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Abstract: *Contemporary mechanisms for the spontaneous formation of glycerol have not been able to explain its existence on early Earth. The exogenous origin and delivery of organic molecules to early Earth presents an alternative route to their terrestrial in situ formation since biorelevant molecules like amino acids, carboxylic acids, and alkylphosphonic acids have been recovered from carbonaceous chondrites. Reported herein is the first in situ identification of glycerol, the key building block of all cellular membranes, formed by exposure of methanol-based — interstellar model ices to ionizing radiation in the form of energetic electrons. These results provide compelling evidence that the radiation-induced formation of glycerol in low-temperature interstellar model ices is facile. Synthesized on interstellar grains and eventually incorporated into the "building material" of solar systems, biorelevant molecules such as glycerol could have been dispensed to habitable planets such as early Earth by comets and meteorites.*

As the central precursor to lipids,[1] glycerol presents the most fundamental unit of prebiotic cell components and to all contemporary cell membranes[2] in living organisms, thus dubbing glycerol as a key molecule pertaining to the origin of life question.[3] The formation of the very first stable membranes has been recognized as the essential prerequisite to the assembly of the earliest self-replicating systems.[4] Understanding the origin of self-replicating systems requires a prior understanding of the formation pathways of lipids and their molecular building blocks (carboxylic acids, phosphorus acids, glycerol).[5] However, contemporary mechanisms for the synthesis of glycerol[6] and the origin of lipids on early Earth involving (mineral catalyzed) hydrothermal conditions have been challenged considering that these molecules are only stable under a narrow range of conditions and cannot form at either low or high pH ranges[7] or in the presence of calcium or magnesium salts[8] which would be present at millimolar concentrations on early Earth. The identification of glycerol together with biorelevant molecules such as amino acids in the Murchison meteorite[9] not only suggests an interstellar origin, but also proposes that glycerol, once formed abiotically, can be delivered to early Earth by meteorites and comets.[10] In addition, phosphite and the membrane biomolecule glycerol phosphate were recently demonstrated to be synthesized under mild thermal conditions with aqueous solutions of glycerol and schreibersite,[11] thus providing soluble phosphorus species necessary for the formation of nucleotides.[12] As such, glycerol is further implicated in the prebiotic synthesis of phosphorylated biomolecules such as RNA as well. These processes can contribute to the inventory of prebiotic compounds, from which cells could have formed and life could have emerged about four billion years ago.[13]

Herein we report the synthesis of glycerol [$HOCH_2CH(OH)CH_2OH$] by exposing low-temperature interstellar model ices to ionizing radiation in the form of energetic electrons as generated in the track of galactic cosmic ray particles. These model ices consist of methanol (CH_3OH) under anhydrous conditions to demonstrate the proof of concept that glycerol can be formed abiotically by interaction of ionizing radiation with methanol ices. Methanol is known to be an important constituent of polar icy mantles of interstellar grains, reaching up to 30% with respect to water, toward young stellar objects AFGL989 and OrionBN.[14] The use of interstellar model ices presents a common approach and initial step as validated by, for instance, Munoz et al.[15] and Bernstein et al.,[16] since no laboratory simulation experiment can mimic the conditions and inherent complexity of interstellar space simultaneously. Therefore, simulation experiments are based on simple models first before extending studies to chemically more complex systems.

Cold molecular clouds are often labeled as nurseries of stars and planetary systems.[14] Here, nanometer-sized grain particles at temperatures as low as 10 K accrete icy layers consisting predominantly of water, methanol, carbon dioxide, and carbon monoxide.[14,17] Through the internal ultraviolet (UV) field and energetic galactic cosmic rays (GCRs), these ices are chemically altered, thus resulting in the formation of complex organic molecules.[18] In star-forming regions, this matter enters circumstellar disks, where formation of planetary bodies takes place, thus also providing the raw material for meteoritic parent bodies.[19] Isotopic studies propose that the material found in carbonaceous chondrites contains a considerable fraction of pristine, interstellar organic matter.[20] Hence organics such as glycerol, which was initially formed in interstellar ices, can be incorporated into meteoritic parent bodies.[21]

The experiments were devised to elucidate potential pathways to synthesize glycerol abiotically upon exposing interstellar model ices (methanol) to ionizing radiation in the form of energetic electrons at radiation doses equivalent to

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[**] We would like to thank the W. M. Keck Foundation, the University of Hawaii and the NASA Exobiology Program MNX13AH62G.

Supporting information for this article (reflectron time-of-flight spectra of the irradiated isotopically labeled ices, infrared spectra of ethylene glycol and glycerol, sublimation profiles of parent methanol molecules and ethylene glycol and the irradiated methanol ice at 160 K and 210 K) is available on the WWW under http://dx.doi.org/10.1002/anie.201408729.

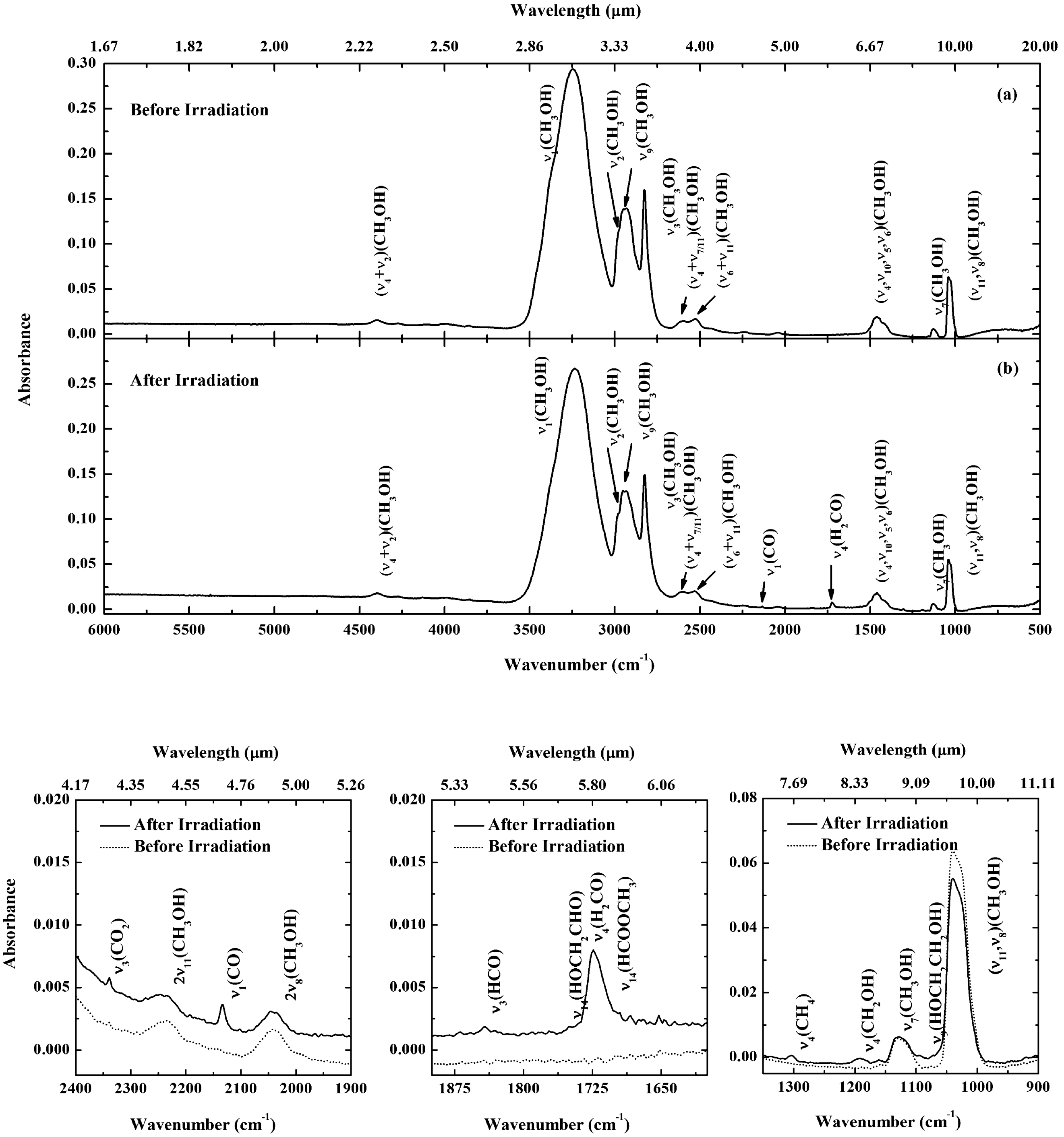

Figure 1. Infrared spectra of the methanol (CH_3OH) ices before (a) and after (b) the irradiation with energetic electrons. The graphics in the lower part of the figure depict the new absorption features in the regions of 2400–1900 cm^{-1}, 1900–1600 cm^{-1}, and 1350–900 cm^{-1}.

the lifetime of molecular clouds. Multiple novel infrared absorptions were observed (Figure 1 a,b) during the irradiation by in situ Fourier Transform infrared (FTIR) spectroscopy. These absorptions were attributed to the formation of eight molecules as follows: carbon monoxide (ν_1; CO: 2135 cm^{-1}; ^{13}CO: 2087 cm^{-1}; $C^{18}O$: 2083 cm^{-1}), carbon dioxide (ν_3; CO_2: 2339 cm^{-1}; $^{13}CO_2$: 2274 cm^{-1}); ketene (ν_2; $H_2{}^{13}C^{13}CO$: 2067 cm^{-1}; $H_2CC^{18}O$: 2107 cm^{-1}), the formyl radical (ν_3; HCO: 1842 cm^{-1}; DCO: 1786 cm^{-1}; $H^{13}CO$: 1797 cm^{-1}), methane (ν_4; CH_4: 1304 cm^{-1}; $^{13}CH_4$: 1296 cm^{-1}; CH_4: 1304 cm^{-1}), formaldehyde (ν_4; H_2CO: 1726 cm^{-1}; D_2CO: 1676 cm^{-1}; $H_2{}^{13}CO$: 1687 cm^{-1}; $H_2C^{18}O$: 1693 cm^{-1}; ν_3; H_2CO: 1499 cm^{-1}; $H_2{}^{13}CO$: 1499 cm^{-1}; $H_2C^{18}O$: 1496 cm^{-1}), the hydroxymethyl radical (ν_4; CH_2OH: 1192 cm^{-1}; $^{13}CH_2OH$: 1167 cm^{-1}; $CH_2{}^{18}OH$: 1168 cm^{-1}), and glycolaldehyde (ν_{14}; $HOCH_2HCO$: 1743 cm^{-1}; $DOCD_2DCO$: 1711 cm^{-1}; $HO^{13}CH_2H^{13}CO$: 1703 cm^{-1}; $H^{18}OCH_2HC^{18}O$: 1713 cm^{-1}; 2 ν_6; $HOCH_2HCO$: 1697 cm^{-1}; $DOCD_2DCO$:

1647 cm^{-1}; $\mathrm{HO^{13}CH_2H^{13}CO}$: 1659 cm^{-1}; $\mathrm{H^{18}OCH_2HC^{18}O}$: 1666 cm^{-1}). Note that the absorption band at 1094 cm^{-1} ($\mathrm{CH_3OH}$ ice), which shifts upon ^{13}C and ^{18}O replacement in the irradiated methanol ices to 928 cm^{-1} and 1015 cm^{-1}, respectively, can be attributed to either ethylene glycol ($\mathrm{HOCH_2CH_2}$; ν_9) and/or glycerol [$\mathrm{HOCH_2CH(OH)CH_2OH}$; ν_{21}]. Considering that the IR spectra of ethylene glycol and glycerol are virtually indistinguishable (see Figure S1 in the Supporting Information) and that the fundamentals of ethylene glycol and glycerol are further obscured by methanol absorptions, it is not feasible to identify glycerol explicitly in the irradiated ices from FTIR spectroscopy alone. Therefore, the complementary technique of single-photon ionization (PI) coupled with reflectron time-of-flight (ReTOF) mass spectrometry is crucial to search for the subliming glycerol in the gas phase.

Temperature-programmed desorption (TPD) after the irradiation results in the sublimation of the synthesized molecules. Here, the subliming, individual molecules are photoionized by 10.49 eV photons. The ions are then extracted into a ReTOF mass spectrometer and mass resolved based on their arrival times. Shown in Figure 2 is the ReTOF mass spectra of the newly formed molecules in the methanol ices recorded as a function of temperature. During the sublimation process, the ice samples were also monitored by IR spectroscopy. After the sublimation of the methanol molecules is complete (see Figure S2), the IR spectrum recorded at 160 K (see Figure S4) depicts characteristic features attributable to the ethylene glycol and/or glycerol molecules, which are free of any interference from the parent methanol precursor. To discriminate if these absorptions belong to ethylene glycol and/or glycerol, the TPD leads to a fractionated sublimation of the ethylene glycol between 185 K and 210 K. This process is monitored by ReTOF by plotting the intensity of the molecular ion of ethylene glycol at m/z 62 ($\mathrm{C_2H_6O_2^+}$) versus the temperature (Figure S2). With the sublimation of ethylene glycol complete at 210 K the corresponding IR spectrum depicts absorptions which can be solely attributed to the glycerol molecules (Figure 1 d). These observations suggest that the interaction of methanol with ionizing radiation synthesizes both ethylene glycol and glycerol, which can be separated by fractionated sublimation.

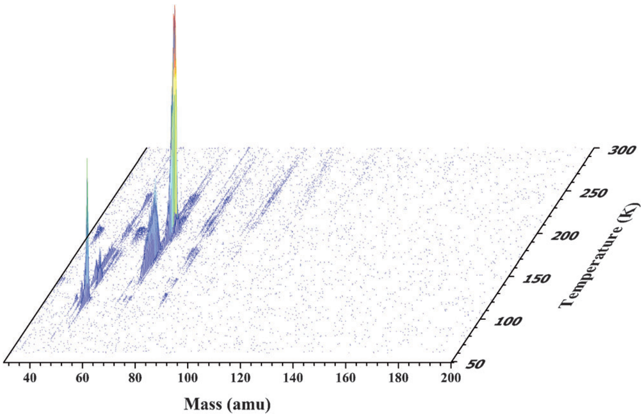

Figure 2. Reflectron time-of-flight (ReTOF) mass spectra as a function of temperature of the newly formed products subliming into the gas phase from radiation processed methanol ice obtained at photoionization energy of 10.49 eV. The absence of signal at mass-to-charges larger than m/z 100 verifies the absence of any glycerol dimers subliming.

To provide further evidence on the formation of glycerol, we present a more in depth analysis of the temperature-dependent ReTOF spectra during the TPD phase at temperatures beyond 210 K. These elevated temperatures result in the sublimation of glycerol and allow gas-phase detection based on the mass-to-charge ratios of the ions and their corresponding shifts upon isotope substitution (D, ^{13}C, ^{18}O). Typically, single-photon ionization of complex organic molecules utilizing vacuum ultraviolet light results in the formation of a single molecular ion without fragments. However, in case of glycerol, the situation is inherently more complex.

Recently, Head-Gordon et al. demonstrated that upon photoionization, glycerol does not only ionize to the glycerol cation ($\mathrm{C_3H_8O_3^+}$; m/z 92), but also undergoes significant dissociative photoionization giving rise to the $\mathrm{C_3H_6O_2^+}$ (m/z 74), $\mathrm{C_2H_6O_2^+}$ (m/z 62), $\mathrm{C_2H_5O_2^+}$ (m/z 61), $\mathrm{C_2H_4O_2^+}$ (m/z 60), $\mathrm{C_2H_5O^+}$ (m/z 45), and $\mathrm{C_2H_4O^+}$ (m/z 44) fragment ions with the parent ion formed at levels of less than a few percent of the total ion counts.[22] Therefore, to verify the formation of glycerol in the present experiments, we have to extract the sublimation profile of glycerol not only by monitoring the parent ion ($\mathrm{C_3H_8O_3^+}$; m/z 92), but also the fragment ions versus the temperature. These sublimation profiles are compiled in Figure 3 for the methanol and isotopically labeled methanol ices, respectively. Within the uncertainty of the experiments, all fragment ions show similar profiles, thus clearly demonstrating that they originate from the same molecule. Also, experiments conducted with isotopically labeled methanol samples demonstrate unambiguously the expected isotopic shifts based on the isotope substitution (D, ^{13}C, ^{18}O). Finally, we integrated the ion counts at distinct mass-to-charge ratios and plotted the integrated ion counts versus the mass-to-charge of the fragment as well as that of the parent ion (Figure 4). A comparison of the graph extracted from our methanol experiment with literature data depicts indistinguishable plots within the error limits. This finding verifies the identification of the glycerol molecule. The data of from the experiments involving isotopic labeling present a similar trend as observed for the methanol ice. Small deviations of the relative intensities exist, and might be attributed to isotope effects in the fragmentation.

The experimental results presented here represent a crucial step toward a systematic understanding of how glycerol (a key component of lipids and cells) can be synthesized in interstellar model ices abiotically by ionizing radiation and transported to Earth. We present here the novel in situ detection of glycerol by exploiting sophisticated analytical techniques under ultra-clean conditions by combining TPD, FTIR spectroscopy, and vacuum ultraviolet single-photon ionization (PI) coupled with ReTOF mass spectrometry. The stability of mineral-embedded sugars and other biorelevant molecules has been established experimentally.[23] Conse-

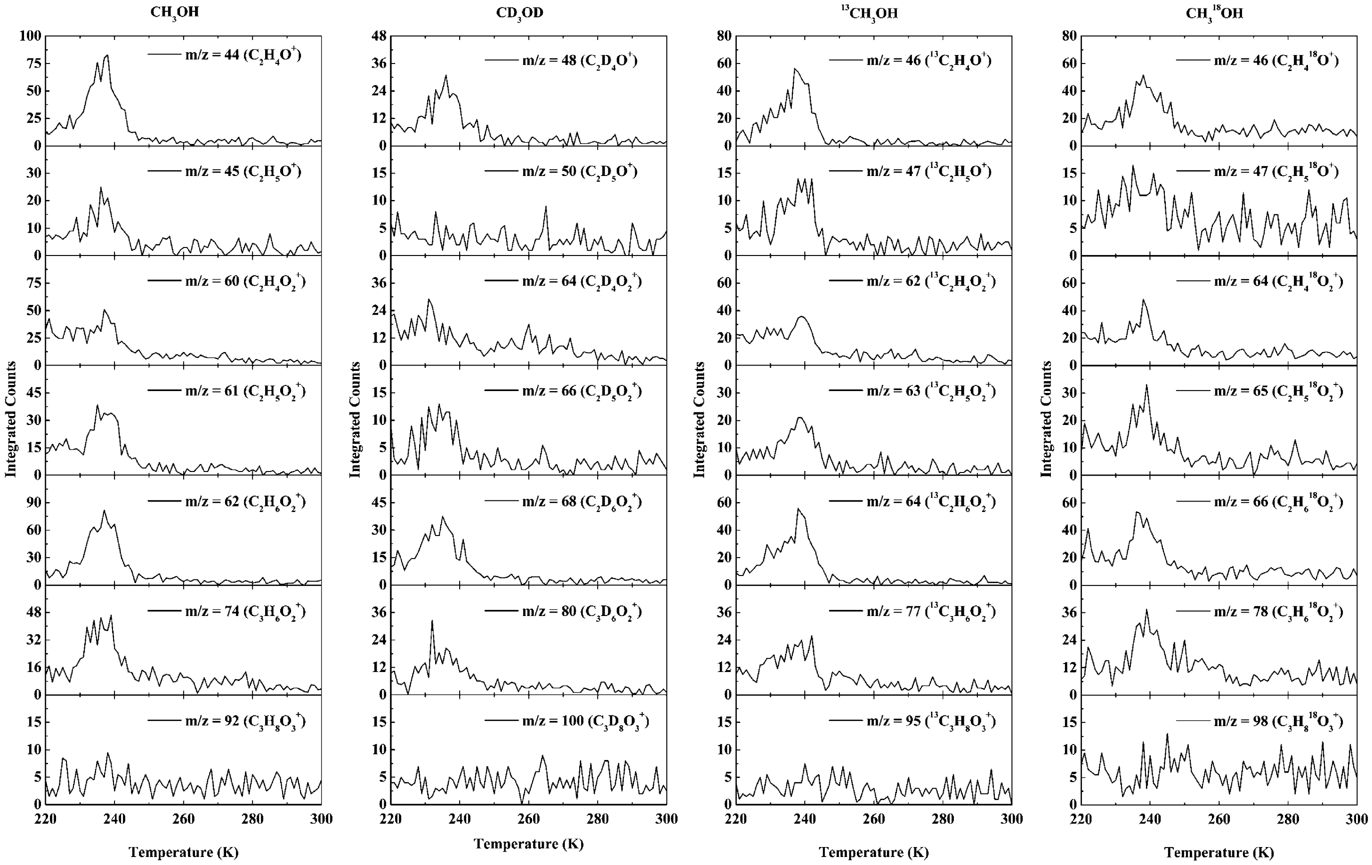

Figure 3. Sublimation profiles of ion counts at mass-to-charges relevant to fragment and parent ions associated with glycerol formation ($C_2H_4O^+$, $C_2H_5O^+$, $C_2H_4O_2{}^+$, $C_2H_5O_2{}^+$, $C_2H_6O_2{}^+$, $C_3H_6O_2{}^+$, $C_3H_8O_3{}^+$) as observed in irradiated CH_3OH, CD_3OD, $^{13}CH_3OH$, and $CH_3{}^{18}OH$ ices obtained at a photoionization energy of 10.49 eV. The pattern for each system suggests that the fragment ions originate from a common parent molecule.

quently, glycerol (once synthesized abiotically under anhydrous conditions from methanol) could have survived on meteoritic parent bodies since their initial formation. Therefore, a small fraction of glycerol on early Earth could have originated from meteorite or comet infall, thus supporting the hypothesis of exoergic source of prebiotic molecules on Earth.[24] This scenario represents a captivating alternative to competing theories such as (mineral-catalyzed) formation of glycerol in hydrothermal vents on early Earth[1,7] and the formose reaction on parent bodies of carbonaceous meteorites requiring aqueous alteration and hence liquid water.[9] So far, glycerol has been detected in the Murchison meteorite, but not in the interstellar medium.

Considering that molecular clouds contain the basic material from which stars and planetary systems are formed, glycerol should be present in the interstellar medium as well. Once synthesized on icy grains, fractions of glycerol could sublime into the gas phase upon transition of the molecular cloud to star-forming regions to be detected by rotational spectroscopy. Since the present experiments form not only glycerol, but also ethylene glycol, it is reasonable to suggest that both molecules should coexist in the gas phase if the temperature of the hot core is sufficient to sublime ethylene glycol and glycerol. Accounting for the ion counts (Figure 4 and Figure S2) and the photoionization cross-sections of ethylene glycol and glycerol, we can estimate relative abundances of 11 ± 2 of ethylene glycol to glycerol with approximately 1 % of the initial methanol converted into glycerol under our experimental conditions. Considering that ethylene glycol has been detected toward SgrB2(N-LMH) at fractions relative to molecular hydrogen of 7×10^{-10},[25] we can predict that glycerol should be present with fractional abundance of about 7×10^{-11} toward the same source. Therefore, the detection of glycerol likely requires the exploitation of powerful telescopes such as the recently commissioned Atacama Large Millimeter/sub-millimeter Array (ALMA).

Unfortunately, because of the overlap of the IR absorptions of ethylene glycol and glycerol, it is difficult to extract information on the formation mechanism in the condensed phase. Based on the structures of the methanol reactant, the potential ethylene glycol intermediate, and the glycerol product, we may propose that the reaction is initiated by the radiolysis of methanol (CH_3OH), thus leading to hydrogen loss and formation of the hydroxymethyl radical (CH_2OH), which was detected by IR spectroscopy. Two methoxy radicals recombine forming the ethylene glycol molecule ($HOCH_2CH_2OH$) as probed by ReTOF. The latter can be radiolyzed and loses a hydrogen atom from the methylene group, thus forming the $HOCH^{\cdot}CH_2OH$ radical, which can then recombine through a barrier-less reaction with a methoxy radical (CH_2OH) and synthesize glycerol. This recombination can either take place at low temperatures if

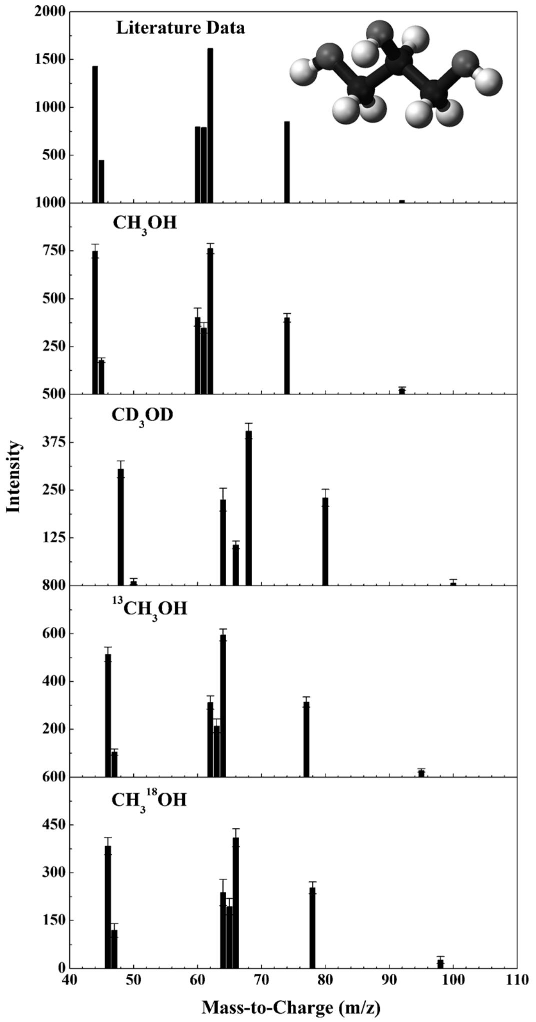

Figure 4. Integrated ion signal at distinct mass-to-charge ratios relevant to fragment and parent ions associated with glycerol formation ($C_2H_4O^+$, $C_2H_5O^+$, $C_2H_4O_2^+$, $C_2H_5O_2^+$, $C_2H_6O_2^+$, $C_3H_6O_2^+$, $C_3H_8O_3^+$) together with their isotopically substituted counterparts in irradiated CH_3OH, CD_3OD, $^{13}CH_3OH$, and $CH_3{}^{18}OH$ ices obtained at a photoionization energy of 10.49 eV. The top graph presents the literature data extracted from ReTOF spectra of glycerol recorded with a photoionization energy of (10.50 ± 0.02) eV.[22] The insert portrays the molecular structure of the glycerol molecule which carbon (black), hydrogen (light gray), and oxygen atoms (dark gray).

both radicals are in the correct geometrical orientation to each other in the ice and/or during the temperature programmed desorption, when the radicals can diffuse in the ice.

Here, we briefly discuss apparent previous ex situ identifications of glycerol in processed astrophysical model ices. Glycerol was first tentatively identified by Agarwal et al. in UV photoprocessed ices at 10 K. However, the authors stated that glycerol and ethylene glycol are likely contaminants from methanol used in the extraction procedure.[26] Glycerol was again later tentatively identified by ex situ GCMS of the residue formed in a similar experimental study on the UV photolysis of ices at 12 K.[27] Again, the authors noted that glycerol was observed as an adventitious contamination. Isotopically labeled ices were then used to bypass the source of contamination, however these results were ambiguous as the photolyzed labeled ices resulted in a mixture of labeled and unlabeled products with intensities which did not match predicted abundances.[27] Finally, glycerol was again proposed to be identified by GCMS analysis of the residue formed through UV photolysis of CH_3OH:NH_3 ice at 80 K, with the use of isotopically labeled ices to again bypass possible sources of contamination.[28] However, the authors specifically mentioned that ethylene glycol was not detected. The fact that ethylene glycol was not detected casts serious doubt on the assignment of glycerol as the formation of ethylene glycol is a precursor reaction necessary in the formation pathway of glycerol and thus should be formed in higher concentrations. Finally, we wish to stress that all previous identifications of glycerol were conducted offline and ex situ using techniques which involve derivatization of functional groups for HPLC or GCMS analysis. Previous experiments have demonstrated that exposure to tholins (residues formed in processed ices with starting chemical compositions relevant to Titan[29]) are chemically altered upon exposure to an oxidizing atmosphere such as our own.[30] As such, the previous identifications may be the result of a contamination and/or secondary reactions upon exposure to an oxygen-rich environment upon venting of the chamber.

To summarize, the present study has provided compelling evidence that the interaction of ionizing radiation in the form of energetic electrons with interstellar model ices of anhydrous methanol followed by annealing the processed ices to 300 K leads to the formation of glycerol—a key molecular building block of lipids which are central components of all cell membranes. Future work will investigate the role of water ice in the formation of glycerol as water is present in actual interstellar ices, possibly acting as an energy-transfer medium and stabilizing matrix. Additionally, a detailed study on how the yield and formation pathways of glycerol depend on distinct interstellar irradiation fields (photons versus galactic cosmic rays) is warranted as is the role of potentially mineral-catalyzed formation routes to glycerol on interstellar ices. These investigations are extremely challenging, but crucial to exploring the basic processes involved in the formation of a key biorelevant molecule—glycerol—in the interstellar medium, thus ultimately exposing molecular processes which might have contributed to the inventory of prebiotic, biorelevant compounds from which cells could have formed and life could have emerged about four billion years ago. Finally, our experimental protocol is designed to identify biorelevant molecules formed under ultra-clean conditions by adapting vacuum ultraviolet single-photon ionization coupled with reflectron time-of-flight mass spectrometry (ReTOF-PI) into space simulation studies and is expected to define a benchmark for future in situ sampling of distinct classes of astrobiologically relevant molecules such as sugars, sugar alcohols, and sugar acids with the ReTOF-PI technique expected to propel astrobiologically related research involving the search for the molecular origin of life in our universe to the next level, ultimately leading to the prediction of an inventory of biorelevant molecules, which could have seeded the evolution of life as we know it.

Received: September 3, 2014

Keywords: ice · interstellar dust · infrared spectroscopy · mass spectrometry · reaction mechanism

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