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Low-Energy Electron-Induced Chemistry of Condensed Methanol: Implications for the Interstellar Synthesis of Prebiotic Molecules

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Abstract

In the interstellar medium, UV photolysis of condensed methanol (CH_3OH), contained in ice mantles surrounding dust grains, is thought to be the mechanism that drives the formation of "complex" molecules, such as methyl formate ($HCOOCH_3$), dimethyl ether (CH_3OCH_3), acetic acid (CH_3COOH), and glycolaldehyde ($HOCH_2CHO$). The source of this reaction-initiating UV light is assumed to be local because externally sourced UV radiation cannot penetrate the ice-containing dark, dense molecular clouds. Specifically, exceedingly penetrative high-energy cosmic rays generate secondary electrons within the clouds through molecular ionizations. Hydrogen molecules, present within these dense molecular clouds, are excited in collisions with these secondary electrons. It is the UV light, emitted by these electronically excited hydrogen molecules, that is generally thought to photoprocess interstellar icy grain mantles to generate "complex" molecules. In addition to producing UV light, the large numbers of low-energy (< 20 eV) secondary electrons, produced by cosmic rays, can also directly initiate radiolysis reactions in the condensed phase. The goal of our studies is to understand the low-energy, electron-induced processes that occur when high-energy cosmic rays interact with interstellar ices, in which methanol, a precursor of several prebiotic species, is the most abundant organic species. Using post-irradiation temperature-programmed desorption, we have investigated the radiolysis initiated by low-energy (7 eV and 20 eV) electrons in condensed methanol at ~ 85 K under ultrahigh vacuum (5×10^{-10} Torr) conditions. We have identified eleven electron-induced methanol *radiolysis* products, which include many that have been previously identified as being formed by methanol UV *photolysis* in the interstellar medium. These experimental results suggest that low-energy, electron-induced condensed phase reactions may contribute to the interstellar synthesis of "complex" molecules previously thought to form exclusively via UV photons.

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1. Introduction

Heat-, photon-, and electron-induced processing provide different routes to initiate chemical reactions. Photochemistry and thermal chemistry may differ because the former is initiated via an excited electronic state while the latter is initiated in the ground electronic state.[1] This difference allows the photosynthesis of products not easily accessed via thermal chemistry. In general, vacuum ultraviolet (VUV) photons (6–12 eV) and low-energy (< 20 eV) electrons will drive similar chemistry given the similarities between photon-induced and electron-induced excitations/ionizations, though yields and product ratios will likely differ. The possible interactions of photons with molecules, however, are restricted by selection rules governed primarily by dipole interactions and spin conservation. For example, photon-induced singlet-to-triplet transitions are nominally forbidden. Electron-induced singlet-to-triplet transitions, however, are allowed because the incident electron can be exchanged with those of the target molecule.[2,d] Furthermore, unlike photons, electrons can be captured into resonant negative ion states that subsequently may dissociate into neutrals and negative ions.[3,4] The interactions of these negative fragments with the parent molecule or other daughter products might yield products unique to electron irradiation. In other words, low-energy, electron-molecule collisions, a fundamental step that occurs during radiation chemistry, could theoretically lead to the synthesis of molecules not accessible via UV photochemistry. Experimental evidence partially supports this claim.[5,6,7]

In addition to the possibility of generating unique molecular species, low-energy, electron-induced chemistry may often predominate over UV photon-induced chemistry depending on the incident flux and the identity and phase of the target molecules. Reaction cross

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[d] It must be noted that selection rules in the condensed phase may differ from those in the gas phase.

sections can be several orders of magnitude larger for electrons than for photons, especially at incident energies corresponding to resonances associated with dissociative electron attachment (DEA), making it easier for electrons to initiate chemical reactions.[e,f] Moreover, electron-induced excitations, in contrast to photon-induced excitations, are not always resonant processes because an incident electron may transfer only the fraction of its energy sufficient to excite the molecule and any excess is removed by the scattered electron.

The dominance of electrons over photons in initiating condensed-phase chemical reactions has been documented for a few molecular species.[8,9,10] Because the chemistry ascribed to photon irradiation in thin films adsorbed on surfaces may be due to substrate photoelectrons, the role of electrons vis-à-vis photons may be underestimated in comparative studies. In this publication, we compare and contrast low-energy, electron-induced reactions with photon-induced reactions of condensed methanol, which is an important component of ice mantles surrounding interstellar grains. Our goal is not only to investigate fundamental differences, but also to identify how such differences impact our understanding of interstellar molecular synthesis.

In recent years, laboratory experiments and theoretical calculations have suggested that UV photon-induced surface and bulk processing of icy grain mantles containing water, carbon monoxide, methanol, and ammonia is one of the main mechanisms for the synthesis of "complex" organic molecules found in hot molecular cores and corinos, the regions within dark, dense molecular clouds warmed by one or more nearby protostars.[11,12,13] The source of UV light that initiates these chemical reactions is thought to be local because externally sourced UV

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[e] Reaction cross sections may, of course, change upon condensation because of intermolecular interactions and the formation of bands structures.

[f] DEA involves the formation of temporary negative ions that subsequently dissociate into neutral species and negatively charged ions.

radiation cannot penetrate these dark, dense molecular clouds. The UV photons are believed to form in these molecular clouds where cosmic rays with energies between 10 and 100 MeV ionize molecular hydrogen to generate secondary electrons each with a mean energy around 30 eV.[14] These low-energy secondary electrons and primary cosmic rays can excite Lyman[g] and Werner band systems of molecular hydrogen.[15] UV light emission from these excited hydrogen molecules is thought to photoprocess icy grain mantles found in dark, dense molecular clouds,[16] leading to the production of radicals both light (e.g., •H) and heavy (e.g., CH_3O•). While facile light radical diffusion is possible at ~10 K,[17] the gradual warm-up from ~10 K to ~100 K in hot cores and hot corinos allows for heavy-radical diffusion. The subsequent barrier-less, radical-radical reactions (i.e., reactions between two open-shell species) lead to the synthesis of "complex" molecules, such as methyl formate ($HCOOCH_3$), which is a potential precursor of biologically important molecules.[18] Building upon early investigations,[19,11] recent laboratory experiments that mimic photochemistry in the interstellar medium have shown that acetaldehyde (CH_3CHO), glycolaldehyde ($HOCH_2CHO$), methyl formate ($HCOOCH_3$), formic acid ($HCOOH$), acetic acid (CH_3COOH), ethylene glycol ($(CH_2OH)_2$), dimethyl ether (CH_3OCH_3), and ethanol (CH_3CH_2OH) can be formed from UV photolysis of condensed methanol.[20]

In addition to producing UV photons, the non-thermal, low-energy, secondary electrons produced by cosmic rays can directly induce radiolysis reactions, a possibility which has been largely ignored in previous astrochemistry studies pertaining to the interstellar medium. Low-energy electrons may result from two processes: (1) the interaction of cosmic rays with gaseous molecular hydrogen present in the dark, dense molecular clouds,[h] and (2) the inelastic collisions

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[g] Not Lyman alpha, which is a spectral line of atomic hydrogen.

[h] These low-energy electrons will interact with only the top few layers of cosmic ices; our experiments simulate these interactions.

that the cosmic ray experiences as it traverses through the ices. Although other high-energy radiolysis secondary products, such as excited species and ions, also cause some radiolytic changes, the inelastic collisions of the low-energy electrons with matter are hypothesized to be the primary driving force in a wide variety of radiation-induced chemical reactions.[21] The majority of these secondary electrons typically have energies below 20 eV.[22] Thus, the goal of our experiments is to investigate directly the processing of astrochemically-relevant laboratory ices by low-energy (≤ 20 eV) electrons characteristic of the secondary electrons produced by the interactions of high-energy radiation, such as cosmic rays, with matter.

Our present work, involving a dedicated quasi-monoenergetic electron gun and a triple-filtered quadrupole mass spectrometer equipped with a pulse ion counting detector, builds upon previous, more limited studies conducted with ~ 50 eV electrons generated from the filament of a mass spectrometer ionizer.[23,24] Only one previous study, involving post-irradiation analysis, has examined the radiolysis of condensed methanol initiated by low-energy (≤ 20 eV) electrons relevant to high-energy radiolysis.[25,26] This study focused on the dynamics of low-energy, electron-induced synthesis of CO from condensed methanol. The results reported herein detail the formation of eleven electron-induced methanol radiolysis products and demonstrate that UV photon and low-energy (≤ 20 eV) electron processing of methanol ices yield essentially the same reaction products. Consequently, our results suggest that cosmic-ray-induced, *low-energy* electrons may also play a role in interstellar molecular synthesis, previously thought to occur exclusively via cosmic-ray-induced UV photons.

2. Experimental

All experiments were conducted in the Wellesley College UHV chamber at base pressures of approximately 5 $\times 10^{-10}$ Torr, described in detail previously.[23] A Mo(110) crystal mounted on a rotary manipulator served as the substrate for all experiments. Rotation of the crystal allowed for positioning in front of the sample doser, electron gun, and mass spectrometer. The crystal was cleaned with an oxygen dose at ~2 $\times$ 10^{-9} Torr for five minutes at ~1200 K, followed by heating to ~2200 K for approximately 30 sec.

The crystal was cooled with liquid nitrogen to ~85 K prior to the introduction of gas samples into the chamber and maintained at this temperature throughout electron irradiation. At this temperature, methanol films condense as amorphous ices. We note that our inability to cool below 85 K limits our ability to detect possible low-energy, electron-induced radiolysis products that have low desorption temperatures. One such possible radiolysis product is ethane (desorption temperature ~ 60 K). Other than this possibility, our inability to cool to 10 K is not a major limitation in studying the relevant chemistry pertaining to ice mantles surrounding dust grains in the interstellar medium. Lower temperatures are not critical because icy dust grains, in regions that become hot cores, are heated from 10 K to temperatures above 100 K by radiation from the ignition of a nearby new star, albeit over a very long time period.[27] Moreover, at temperatures around 10 K diffusion of heavy radicals such as CH_3O is unlikely, precluding radical-radical reactions that are likely routes to “complex” molecules. Interestingly, astrochemically-relevant ice analogs grown at liquid nitrogen temperature are studied at University College London.[27]

Samples were introduced into the UHV chamber through a precision leak valve. Samples other than methanol were only used for temperature-programmed desorption control experiments involving no prior electron irradiation. Samples were obtained from Sigma-Aldrich (methanol, HPLC grade 99.9%; methanol, anhydrous, 99.8%; glycolaldehyde dimer; ethylene glycol 99.8%; methyl formate, anhydrous 99%), EMD (glacial acetic acid), Fluka (formic acid, ~98%) and Pharmco-AAPER (absolute ethanol, ACS/USP grade). Liquid/solid samples were transferred under a nitrogen atmosphere to Schlenk tubes, and degassed by three freeze-pump-thaw cycles. Mixtures of methanol and a suspected radiolysis product were prepared semi-quantitatively and dispensed from a single Schlenk tube. The mixture of methanol and glycolaldehyde was warmed slightly before introduction into the UHV chamber in order to ensure that the glycolaldehyde was introduced in its monomeric form.

Results of a series of temperature-programmed desorption experiments conducted in the absence of electron irradiation were used to estimate the coverage of methanol. One monolayer is defined as the maximum exposure of methanol that does not yield a multilayer peak. Film thicknesses on the Mo(110) crystal were controlled by monitoring the dosing chamber pressure drop, as measured by an MKS Baratron capacitance manometer.

Methanol films were irradiated using a Kimball Physics FRA2X1-2 flood electron gun (cathode terminal spread of 0.4 eV). The incident current on the clean crystal was set at 2 μA (flux = 2×10^{13} electrons/cm^2/s) for all electron irradiation experiments. The crystal was grounded during electron bombardment to minimize charging of the adsorbate thin film. After irradiation, temperature-programmed desorption measurements were performed using a Hiden IDP Series 500 quadrupole mass spectrometer. To optimize the signal-to-noise ratio, no more than five masses were monitored during typical temperature-programmed desorption experiments. Temperature-programmed desorption experiments conducted in the absence of electron irradiation served as control experiments. Surface temperature was monitored using a W/5% Re vs. W/26% Re thermocouple spot welded to the edge of the crystal.

3. Results and Discussion

3.1 Identification of Radiolysis Products.

The electron-induced radiolysis products of condensed methanol were identified using the results of post-irradiation temperature-programmed desorption experiments. We have previously shown that the effects of low-energy electrons on condensed-phase molecules can be investigated by temperature-programmed desorption experiments conducted following low-energy electron irradiation of nanoscale thin films.[23] Post-irradiation temperature-programmed desorption is ideal for analyzing complex mixtures because radiolysis products can be separated based on desorption temperature. This technique is also very sensitive, allowing the detection of submonolayer quantities as low as 0.005 ML.

The experimental data were analyzed by comparing mass spectral fragments observed during thermal desorption to known mass spectra.[28] When identification of a particular radiolysis product was uncertain, temperature-programmed desorption data for methanol films containing that suspected radiolysis product were used as reference. Results of analogous experiments with methanol isotopologues ($^{13}CH_3OH$ and CD_3OD) also were used in product identification. Because there is usually a correlation between boiling points and multilayer desorption temperatures, this trend was used as tertiary evidence for product identification. Mass-to-charge ratios greater than 75 were not usually monitored because such fragments are not likely to be from nascent radiolysis products.

Because of the multitude of methanol radiolysis products whose yields were dependent on film thickness, irradiation time, and incident electron energy, several hundred post-irradiation temperature-programmed desorption experiments were conducted to help identify the electron-induced radiolysis products of methanol. The very small radiolysis yields and the closeness in desorption temperatures required that no more than five mass spectral fragments be monitored during temperature-programmed desorption experiments. Despite these precautions, all mass-to-charge ratios that evince peaks at a given temperature cannot be assumed to represent desorption of a single product. In addition, because of detector saturation, it was not possible to monitor mass spectral fragments (e.g., $m/z = 31$) that were common to both methanol and some radiolysis products. Because of the reasons enumerated above, several of our identifications of low-energy electron-induced methanol radiolysis products are not unambiguous.

Results of temperature-programmed desorption experiments conducted following irradiation of condensed $^{12}CH_3OH$ with 7 eV and 20 eV electrons are shown in Figures 1 and 2, respectively.[i] All experiments for Figures 1 and 2 were conducted with a film thickness of 20 ML and a flux of 2×10^{13} electrons/cm^2/s and a fluence of 3×10^{13} electrons/cm^2. Each figure represents a composite of several experiments conducted under identical conditions. To improve clarity, not all mass spectral fragments monitored are shown in these two figures. Results of a temperature-programmed desorption experiment conducted following irradiation of condensed $^{13}CH_3OH$ with 20 eV electrons are shown in Figure 3.

The identifications of the eleven electron-induced methanol radiolysis products ((A) formaldehyde (H_2CO), (B) dimethyl ether (CH_3OCH_3), (C) methyl formate ($HCOOCH_3$), (D) acetaldehyde (CH_3CHO), (E) glycolaldehyde ($HOCH_2CHO$), (F) acetic acid (CH_3COOH), (G) ethanol (CH_3CH_2OH), (H) methoxymethanol (CH_3OCH_2OH), (I) ethylene glycol ($(CH_2OH)_2$), (J) glycolic acid ($HOCH_2CO_2H$), and (K) 1, 2, 3-propanetriol ($HOCH_2CHOHCH_2OH$)) are discussed in detail below.

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[i] 7 eV is below the ionization energy of methanol. The preponderance of electrons resulting from the interaction of high-energy radiation with condensed matter has energies below 20 eV.

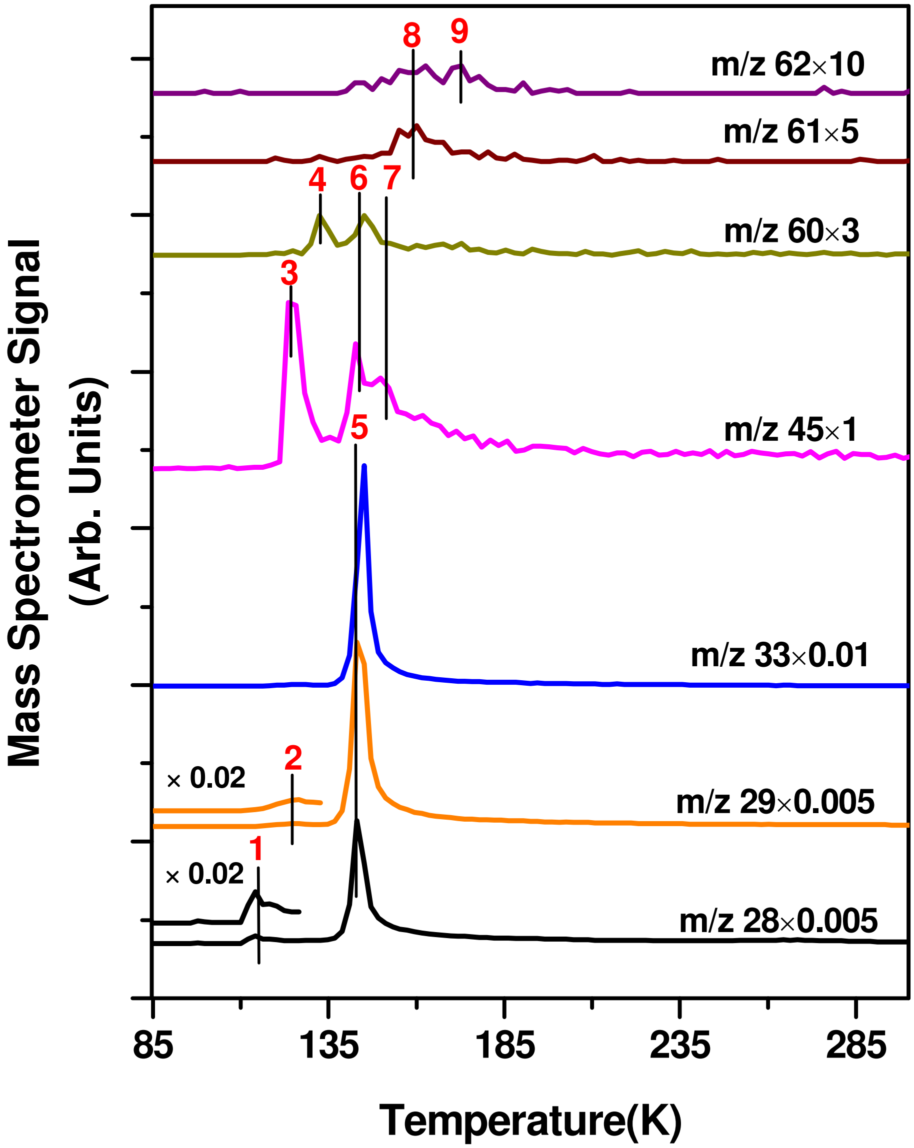

Figure 1

Post irradiation temperature-programmed desorption data for 20 monolayers of $^{12}CH_3OH$ irradiated with 7 eV electrons for 20 minutes at an incident current of 2 μA (flux = 2 × 10^{13} electrons/cm^2/s and fluence = 3 × 10^{13} electrons/cm^2) shows several desorption features: (1) CO (background), (2) formaldehyde (H_2CO), (3) dimethyl ether (CH_3OCH_3), (4) methyl formate ($HCOOCH_3$), (5) methanol (CH_3OH), (6) glycolaldehyde ($HOCH_2CHO$), (7) ethanol (CH_3CH_2OH) and acetic acid (8) methoxymethanol (CH_3OCH_2OH), (9) ethylene glycol ($(CH_2OH)_2$). Plots vertically offset for clarity.

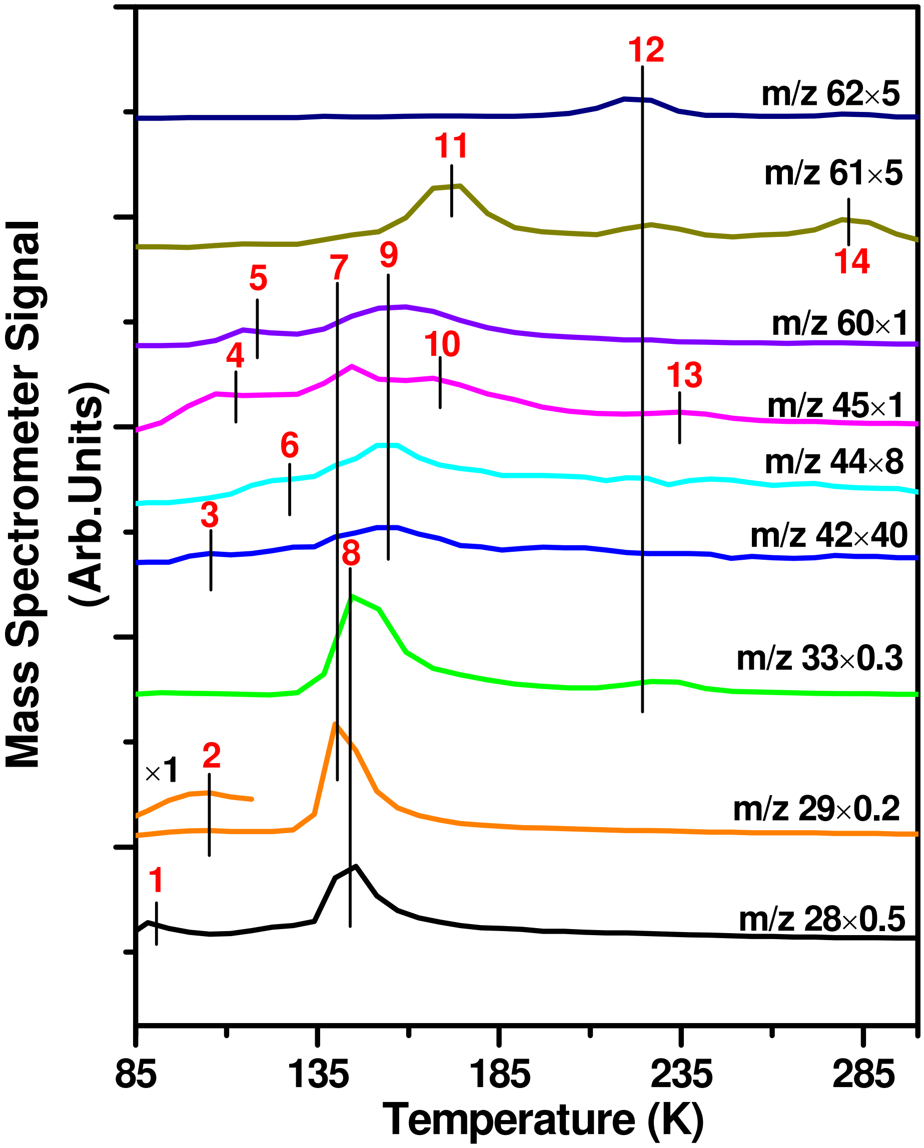

Figure 2

Post irradiation temperature-programmed desorption data for 20 monolayers of $^{12}CH_3OH$ irradiated with 20 eV electrons for 20 minutes at an incident current of 2 μA (flux = 2 × 10^{13} electrons/cm^2/s and fluence = 3 × 10^{13} electrons/cm^2) shows several desorption features: (1) CO (background), (2) formaldehyde (H_2CO), (3) unknown, (4) dimethyl ether (CH_3OCH_3), (5) methyl formate ($HCOOCH_3$), (6) acetaldehyde (CH_3CHO), (7) glycolaldehyde ($HOCH_2CHO$), (8) methanol (CH_3OH), (9) acetic acid (CH_3COOH), (10) ethanol (CH_3CH_2OH), (11) methoxymethanol (CH_3OCH_2OH), (12) ethylene glycol ($(CH_2OH)_2$), (13) glycolic acid ($HOCH_2CO_2H$), (14) 1, 2, 3-propanetriol ($HOCH_2CHOHCH_2OH$). Plots vertically offset for clarity.

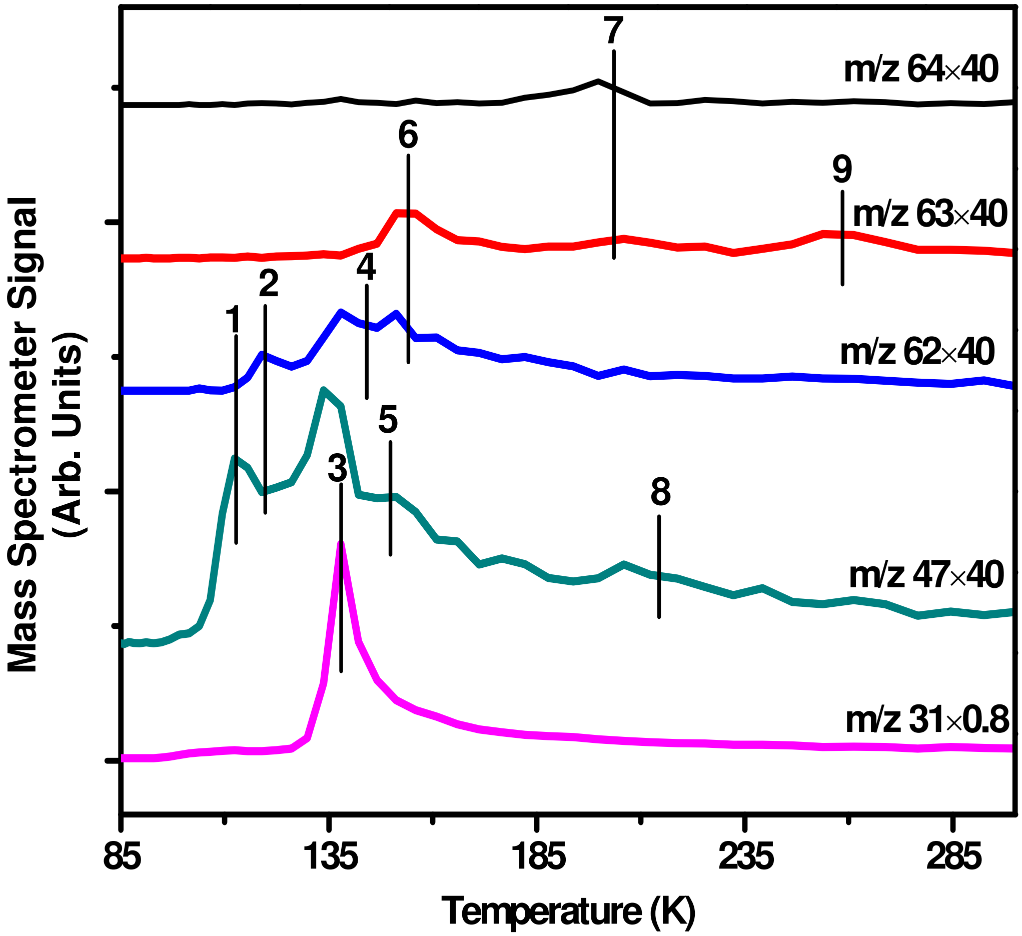

Figure 3

Post irradiation temperature-programmed desorption data for 20 monolayers of $^{13}CH_3OH$ irradiated with 20 eV electrons for 20 minutes at an incident current of 2 μA (flux = 2×10^{13} electrons/cm^2/s and fluence = 3×10^{13} electrons/cm^2) shows several desorption features: (1) dimethyl ether (CH_3OCH_3), (2) methyl formate ($HCOOCH_3$), (3) methanol (CH_3OH), (4) acetic acid (CH_3COOH), (5) ethanol (CH_3CH_2OH), (6) methoxymethanol (CH_3OCH_2OH), (7) ethylene glycol ($(CH_2OH)_2$), (8) glycolic acid ($HOCH_2CO_2H$), (14) 1, 2, 3-propanetriol ($HOCH_2CHOHCH_2OH$). Plots vertically offset for clarity. The positioning of the vertical lines labeled 4 and 8 is somewhat arbitrary.

A. Identification of Formaldehyde (H_2CO)

A very small peak identified as evidence of formaldehyde was seen for *m*/*z* = 29 [CHO^+] at ~115 K in post-irradiation temperature programmed desorption experiments (Figures 1–2). The fragment *m*/*z* = 29 is the dominant ion in the formaldehyde mass spectrum.[28] Results of isotopic labeling experiments with $^{13}CH_3OH$ provided additional evidence for the identification of formaldehyde (data not shown). Formaldehyde has been identified as a photolysis/radiolysis product of methanol following irradiation with UV light,[11, 19-20] 55 eV electrons,[23] 1 keV electrons (tentative),[29] 5 keV electrons,[30] 1 MeV protons,[31] and 3 keV He^+ ions.[32]

B. Identification of Dimethyl Ether (CH_3OCH_3)

Results of post-irradiation temperature programmed desorption experiments of methanol ($^{12}CH_3OH$) displayed at ~115 K for *m*/*z* = 45 [$C_2H_5O^+$] (Figures 1–2) and *m*/*z* = 46 [$C_2H_6O^+$] (data not shown) desorption peaks, which we assign to dimethyl ether (CH_3OCH_3). The fragments *m*/*z* = 45 and *m*/*z* = 46 are the dominant ions in the dimethyl ether mass spectrum.[28] As shown in Figure 3, a peak for *m*/*z* = 47 [$^{13}C_2H_5O^+$] was observed at approximately the same temperature in post-irradiation temperature programmed desorption experiments involving $^{13}CH_3OH$. These post-irradiation temperature programmed desorption results were consistent with those of temperature-programmed desorption experiments involving unirradiated 2:1 mixture of methanol and dimethyl ether, providing additional support for the identification of dimethyl ether as a low-energy, electron-induced radiolysis product of condensed methanol. This identification is further verified by the desorption temperatures of dimethyl ether and formaldehyde being approximately the same, consistent with their boiling points of 251 K and

254 K, respectively. Irradiation of condensed methanol with UV light[20] and 55 eV electrons[23] has been previously shown to yield dimethyl ether.

C. Identification of Methyl Formate ($HCOOCH_3$)

The identification of methyl formate was based on results of post-irradiation temperature programmed desorption experiments that evinced peaks at ~120 K for $m/z = 60$ [$C_2H_4O_2^+$] (Figures 1–2). Coincident peaks were also observed in some post-irradiation experiments for $m/z = 42$ [$C_2H_2O^+$], $m/z = 29$ [HCO^+], and $m/z = 28$ [CO^+] (Figures 2). Following $m/z = 31$[H_2CO^+],[j] the fragments $m/z = 60$, 29, and 28 are the three most significant ions in the methyl formate mass spectrum.[28] As shown in Figure 3, a peak for $m/z = 62$ [$^{13}C_2H_4O_2^+$] was observed at approximately the same temperature in post-irradiation temperature-programmed desorption experiments involving $^{13}CH_3OH$. The identification methyl formate was further corroborated by results of temperature-programmed desorption experiments involving unirradiated 1:1 mixtures of methyl formate and methanol (data not shown). The desorption temperature of methyl formate is above that of dimethyl ether, consistent with their boiling points of 305 K and 251 K, respectively. However, the observed desorption temperatures of methyl formate and acetaldehyde (boiling point 294 K) are not consistent with their boiling points. Methyl formate has been identified as a photolysis/radiolysis product of condensed methanol following irradiation with UV light,[11, 20] 55 eV electrons (tentative),[24] 1 keV electrons (tentative),[29] and 5 keV electrons.[30]

D. Identification of Acetaldehyde (CH_3CHO)

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[j] Fragment $m/z = 31$, which is also the dominant ion for methanol, cannot be monitored in our experiments because of detector saturation.

Results of temperature-programmed desorption experiments conducted following low-energy (20 eV) electron irradiation of condensed CH_3OH demonstrated at ~ 120 K for *m*/*z* =44 [$C_2H_4O^+$] (Figure 2), *m*/*z* =43 [$C_2H_3O^+$] (data not shown), and *m*/*z* =42 [$C_2H_2O^+$] (Figure 2) desorption features which we attribute to acetaldehyde (CH_3CHO). The fragments *m*/*z* = 44, 43, and 42 are three significant ions in the published mass spectrum of acetaldehyde.[28] The desorption temperature of acetaldehyde is below that of methanol, consistent with their boiling points of 294 K and 337 K, respectively. Clear evidence was absent for the formation of acetaldehyde following 7 eV electron irradiation of methanol (Figure 1). Acetaldehyde has been previously identified as a UV photolysis product of condensed methanol.[20]

E. Identification of Glycolaldehyde ($HOCH_2CHO$)

We attribute to glycolaldehyde (hydroxy acetaldehyde) ($HOCH_2CHO$) desorption features seen for *m*/*z* = 60 [$C_2H_4O_2^+$], *m*/*z* = 42 [$C_2H_2O^+$], and *m*/*z* = 29 [CHO^+] at ~140 K in post-irradiation temperature-programmed desorption experiments (Figures 1 and 2). The fragments *m*/*z* = 60, 42, and 29 are three significant ions in the published mass spectrum of glycolaldehyde.[28] This identification of glycolaldehyde is also consistent with results (data not shown) of post-irradiation temperature-programmed desorption experiments conducted with the isotopologue $^{13}CH_3OH$ and (2) temperature-programmed desorption experiments involving no prior irradiation of methanol and glycolaldehyde mixtures. Irradiation of condensed methanol with 55 eV electrons (tentative),[24] 5 keV electrons,[30] and UV photons[20] has been shown to yield glycolaldehyde.

F. Identification of Acetic Acid (CH_3COOH)

The identification of acetic acid is based on post-irradiation temperature programmed desorption results that evinced desorption peaks at ~ 155 K for *m/z* = 60 [$C_2H_4O_2^+$], *m/z* = 45 [$COOH^+$], *m/z* = 44 [$C_2H_4O^+$ or CO_2^+], and *m/z* = 42 [$C_2H_2O^+$] (Figure 2). A desorption peak at the same temperature was also observed for *m/z* = 43 [$C_2H_3O^+$] (data not shown). The fragments *m/z* = 60, 45, and 43 are the three most significant ions in the published mass spectrum of acetic acid.[28] As shown in Figure 3, a peak for *m/z* = 62 [$^{13}C_2H_4O_2^+$] was observed at approximately the same temperature in post-irradiation temperature-programmed desorption experiments involving $^{13}CH_3OH$. Additional evidence to support this identification was provided by results (data not shown) of temperature-programmed desorption experiments involving unirradiated thin films containing mixtures of methanol and acetic acid. We attribute the lower desorption temperature of acetic acid (b.p. 391 K) relative to that of ethanol (b.p. 351 K) (Figure 2) to the likely absence of acetic acid dimers in the irradiated methanol. Previous experiments have demonstrated that the UV photolysis of condensed methanol also yields CH_3COOH.[20]

G. Identification of Ethanol (CH_3CH_2OH)

We attribute to ethanol the peak at ~ 165 K for *m/z* = 46 [$CH_3CH_2OH^+$] (Figure 2) observed during temperature-programmed desorption experiments conducted following irradiation of methanol with 20 eV electrons. Desorption peaks (data not shown) at the same temperature were also observed for *m/z* = 43 [$C_2H_3O^+$], *m/z* = 44 [$C_2H_3O^+$] and *m/z* = 45 [$CH_3CH_2O^+$]. The fragments *m/z* = 46, 45, and 43 are three significant ions in the published mass spectrum of ethanol.[28] As shown in Figure 3, a peak for *m/z* = 47 [$^{13}C_2H_5O^+$] was observed at approximately the same temperature in post-irradiation temperature-programmed desorption experiments involving $^{13}CH_3OH$. Ethanol has been previously identified as a low-energy electron-induced radiolysis[23] and a UV-photolysis[20] product of condensed methanol.

H. Identification of Methoxymethanol (CH_3OCH_2OH)

Methoxymethanol was identified as a product following irradiation of condensed methanol with low-energy electrons. This identification was based on peaks for *m/z* = 61 [$CH_3OCH_2O^+$] and *m/z* = 62 [$CH_3OCH_2OH^+$] at ~165 K observed in the results of post-irradiation temperature-programmed desorption experiments (Figures 1 and 2). Our results are consistent with the published mass spectrum[33] of methoxymethanol, a highly labile species for which a mass spectrum is not found in standard tables.[28] As shown in Figure 3, a peak for *m/z* = 63 [$^{13}C_2H_5O_2^+$] was observed at approximately the same temperature in post-irradiation temperature-programmed desorption experiments involving $^{13}CH_3OH$. The boiling points of methoxy methanol (356 K, estimated[k]), ethanol (351 K), and ethylene glycol (470 K) are consistent with the trends observed in the desorption temperatures for these three species. Methoxymethanol was previously identified following irradiation of condensed methanol with 55 eV electrons,[23] but not following irradiation with UV light,[11, 20] 1 keV electrons,[29] or 5 keV electrons.[30]

I. Identification of Ethylene Glycol ($HOCH_2CH_2OH$)

We attribute to ethylene glycol ($HOCH_2CH_2OH$) desorption features seen for *m/z* = 33 [CH_5O^+], *m/z* = 44 [$C_2H_3O^+$], *m/z* = 61 [$OCH_2CH_2OH^+$], and *m/z* = 62 [$HOCH_2CH_2OH^+$] at ~ 215 K in post-irradiation temperature-programmed desorption experiments (Figure 2). These four mass-to-charge ratios are significant mass spectral fragments of ethylene glycol.[28] As shown

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[k] CSID:56311, http://www.chemspider.com/Chemical-Structure.56311.html (accessed 14:23, Dec 21, 2013)

in Figure 3, a peak for *m/z* = 63 [$^{13}C_2H_5O_2^+$] was observed at approximately the same temperature in post-irradiation temperature-programmed desorption experiments involving $^{13}CH_3OH$. Ethylene glycol's boiling point (470 K) and desorption temperature are consistent with this identification. Results of previous experiments have demonstrated that γ-radiolysis,[34] low-energy electron-induced radiolysis,[23] 5 keV electron-induced radiolysis,[30] and UV photolysis[20] of condensed methanol also yield ethylene glycol. Results of temperature-programmed desorption experiments involving no prior irradiation of methanol and ethylene glycol were used in our previous identification of ethylene glycol as a radiolysis product of methanol.[23]

J. Identification of Glycolic acid ($HOCH_2COOH$)

Glycolic acid (hydroxyacetic acid) ($HOCH_2COOH$) was tentatively identified as a product following irradiation of condensed methanol with 20 eV electrons. This identification was based on a peak for *m/z* = 45 [$COOH^+$] at ~235 K observed in the results of post-irradiation temperature-programmed desorption experiments (Figure 2). The absence of peaks for *m/z* = 60 and *m/z* = 75 at the same temperature is consistent with the miniscule signals for these fragments in the published mass spectrum of glycolic acid.[28] As shown in Figure 3, a possible peak for *m/z* = 47 [$^{13}CHO_2^+$] was observed at approximately the same temperature in post-irradiation temperature-programmed desorption experiments involving $^{13}CH_3OH$. The boiling points of glycolic acid (538 K, estimated[l]) and ethylene glycol (470 K) are consistent with the trend in desorption temperatures for these two species. Glycolic acid has never been previously identified as a radiolysis/photolysis product of pure condensed methanol. Glycolic acid is likely a

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[l] CSID:737, http://www.chemspider.com/Chemical-Structure.737.html (accessed 22:18, Dec 21, 2013)

radiolysis product of a methanol radiolysis product, not a nascent *primary* radiolysis product of methanol. Interestingly, no evidence was seen for the formation of glycolic acid following irradiation of a 5 ML thick methanol film.

K. Identification of 1,2,3-Propanetriol ($HOCH_2CHOHCH_2OH$)

The tentative identification of 1,2,3-propanetriol (glycerin) (glycerol) ($HOCH_2CHOHCH_2OH$) is based on post-irradiation temperature programmed desorption results that evinced desorption peaks at ~ 280 K for $m/z = 43$ [$C_3H_7^+$], $m/z = 61$[$C_2H_5O_2^+$], and $m/z = 75$ [$C_3H_7O_2^+$] (Figure 2). As shown in Figure 3, a peak for $m/z = 63$ [$^{13}C_2H_5O_2^+$] was observed at approximately the same temperature in post-irradiation temperature programmed desorption experiments involving $^{13}CH_3OH$. The boiling points of glycerol (563 K, estimated), glycolic acid (538 K), ethylene glycol (470 K) are consistent with the trends observed in the desorption temperatures for these three species. Although previously identified as a radiolysis product of methanol,[35] glycerol is likely not a nascent *primary* radiolysis product of methanol. Post-irradiation temperature programmed desorption experiments did not show evidence for the formation of glycerol following irradiation of a 5 ML thick methanol film.

L. Non-Identification of Other Predicted Radiolysis Products

Clear evidence was absent for the formation of several expected radiolysis products ((see Table 1): ethane (CH_3CH_3), dimethyl peroxide (CH_3OOCH_3), glyoxal ($CHOCHO$), methylene glycol ($HOCH_2OH$), methyl hydroperoxide (CH_3OOH), and formic acid ($HCOOH$).

Radical 1 **Radical 2**	**•CH_2OH**	**•HCO**	**CH_3O•**	**•CH_3**	**•OH**	**•H**
•CH_2OH	$HOCH_2CH_2OH$ Ethylene Glycol	CH_2OHCHO Glycolaldehyde	CH_3OCH_2OH Methoxymethanol	CH_3CH_2OH Ethanol	$HOCH_2OH$ Methylene Glycol	CH_3OH Methanol
•HCO	CH_2OHCHO Glycolaldehyde	CHOCHO Glyoxal	CH_3OCHO Methyl Formate	CH_3CHO Acetaldehyde	HCOOH Formic Acid	H_2CO Formaldehyde
CH_3O•	CH_3OCH_2OH Methoxymethanol	CH_3OCHO Methyl Formate	CH_3OOCH_3 Dimethyl Peroxide	CH_3OCH_3 Dimethyl Ether	CH_3OOH Methyl Hydroperoxide	CH_3OH Methanol
•CH_3	CH_3CH_2OH Ethanol	CH_3CHO Acetaldehyde	CH_3OCH_3 Dimethyl Ether	CH_3CH_3 Ethane	CH_3OH Methanol	CH_4 Methane
•OH	$HOCH_2OH$ Methylene Glycol	HCOOH Formic Acid	CH_3OOH Methyl Hydroperoxide	CH_3OH Methanol	HOOH Hydrogen Peroxide	H_2O Water
•H	CH_3OH Methanol	H_2CO Formaldehyde	CH_3OH Methanol	CH_4 Methane	H_2O Water	H_2 Dihydrogen

Table 1

Possible radiolysis products of methanol based on expected radical-radical reactions. This compendium is an extension of a previously published table.[30]

3.2 Proposed reaction mechanisms for low-energy, electron-induced radiolysis of methanol

The synthesis of radiolysis products at incident electron energies as low as 7 eV indicates that electron impact ionization is not the only mechanism through which low-energy, electrons initiate reactions in the methanol thin films. Results of our recent[36] study of the low-energy electron-induced formation of ethylene glycol and methoxymethanol are consistent with a radical-radical reaction mechanism. The absence of resonant structures in plots of the yield vs. incident electron energy suggest that non-resonant electron impact excitation is the primary mechanism by which electrons initiate methoxy methanol and ethylene glycol formation below the ionization threshold. Moreover, the functional forms for the radiolysis yields vs. fluence are well fit by a quadratic function indicating that two independent dissociation events lead to the formation of both methoxymethanol and ethylene glycol.[36] Based on these results, we propose the following mechanism involving formation of methoxy ($CH_3O\bullet$) and hydroxymethyl ($\bullet CH_2OH$) radicals via electron impact excitation followed by radical-radical coupling:

$$\mathrm{CH_3OH} \xrightarrow{e^-} \left[\mathrm{CH_3OH}\right]^* + e^- \quad (1)$$

$$\left[\mathrm{CH_3OH}\right]^* \longrightarrow \bullet\mathrm{CH_2OH} + \bullet\mathrm{H} \quad (2)$$

$$\left[\mathrm{CH_3OH}\right]^* \longrightarrow \bullet\mathrm{CH_3O} + \bullet\mathrm{H} \quad (3)$$

$$\mathrm{CH_3O}\bullet + \bullet\mathrm{CH_2OH} \longrightarrow \mathrm{CH_3OCH_2OH} \quad (4)$$

$$\bullet\mathrm{CH_2OH} + \bullet\mathrm{CH_2OH} \longrightarrow \mathrm{HOCH_2CH_2OH} \quad (5)$$

As shown in Table 1, mechanisms involving the coupling of the expected radicals ($\bullet CH_2OH$, $\bullet HCO$, $CH_3O\bullet$, $\bullet CH_3$, $\bullet OH$, and $\bullet H$) may account for the formation of all observed products except those that are likely not primary methanol radiolysis products (acetic acid (CH_3COOH), glycolic acid ($HOCH_2COOH$), and 1,2,3-propanetriol ($HOCH_2CHOHCH_2OH$). Radical-radical reaction mechanisms are plausible given the formation of all primary radiolysis products (except perhaps acetaldehyde) at an incident electron energy of 7 eV, below the ionization energy for methanol.

3.3 Comparison to high-energy radiolysis of methanol

All four previously published high-energy (arbitrarily defined as 1 keV or higher) radiolysis studies involving methanol thin films were conducted using post-irradiation infrared-reflection absorption spectroscopy (IRAS).[29,30, 32,37] These studies involved the irradiation of condensed methanol with either 1–5 keV electrons or 3 keV He^+ ions. As detailed in Table 2, no study identified more than six methanol radiolysis products. We attribute this low number of identified radiolysis products to the lower sensitivity of IRAS compared to TPD. Moreover, post-irradiation temperature-programmed desorption is perhaps better for analyzing complex mixtures because radiolysis products are separated by temperature. All four studies identified formaldehyde, methane, carbon dioxide, and carbon monoxide as high-energy radiolysis products of condensed methanol. Only one study identified the production of two-carbon species such as methyl formate and ethylene glycol.[30] Results of our preliminary unpublished experiments indicate that high-energy (~ 900 eV electron) radiolysis of methanol yields the same products as those reported herein, consistent with the hypothesis that high-energy radiolysis in condensed matter is mediated by low-energy electrons.

Radiolysis Products	**This Work**	**Arumainayagam (1995)[23]**	**Sanche (1997)[25,26]**	**White (1997)[24]**	**Mason (2013)[29]**	**Kaiser (2007)[30]**	**Palumbo (1999)[37]**	**Baratta (2002)[32]**	**Allamandola (1988)[19]**	**Öberg (2009)[20]**		**Gerakines (1996)[11]**
	20 eV electrons	**55 eV electrons**	**0-20 eV electrons**	**52 eV electrons**	**1 keV electrons**	**5 keV electrons**	**3 keV He^+ ions**	**3 keV He^+ ions**	**UV photolysis**	**UV photolysis**		**UV photolysis**
	TPD	**TPD**	**HREELS**	**IRAS**	**IRAS**	**IRAS**	**IRAS**	**IRAS**	**IR**	**TPD**	**IR**	**IRAS**
Formaldehyde H_2CO	Y	Y		Y	Y	Y	Y	Y	Y	Y	Y	Y
Dimethyl ether CH_3OCH_3	Y	Y								Y	Y	
Methyl formate $HCOOCH_3$	Y			Y		Y				Y	Y	Y
Acetaldehyde CH_3CHO	Y									Y	Y	
Glycolaldehyde $HOCH_2CHO$	Y			Y		Y				Y	Y	
Acetic acid CH_3COOH	Y									Y	Y	
Ethanol CH_3CH_2OH	Y	Y								Y	Y	Y
Methoxymethanol CH_3OCH_3OH	Y	Y										
Ethylene glycol $(CH_2OH)_2$	Y	Y				Y				Y	Y	Y
Glycolic acid $HOCH_2CO_2H$	Y											
Glycerol $HOCH_2CHOHCH_2OH$	Y											
Carbon monoxide CO			Y		Y	Y	Y	Y	Y		Y	Y
Methane CH_4				Y	Y	Y	Y	Y	Y		Y	Y
Carbon dioxide CO_2					Y	Y	Y	Y	Y			Y
Formic acid HCOOH										Y		

Table 2

Compendium of radiolysis/photolysis products of condensed methanol identified by post-irradiation temperature programmed desorption (TPD), infrared-reflection absorption spectroscopy (IRAS), and high resolution electron energy loss spectroscopy (HREELS).

3.4 Low-energy electrons vs. UV photons

Of special interest is the comparison of electron-induced and photon-induced condensed-phase methanol reactions. Recent results of post-irradiation temperature-programmed desorption experiments indicate that acetaldehyde (CH_3CHO), glycolaldehyde ($HOCH_2CHO$), methyl formate ($HCOOCH_3$), formic acid ($HCOOH$), acetic acid (CH_3COOH), ethylene glycol ($(CH_2OH)_2$), dimethyl ether (CH_3OCH_3), and ethanol (CH_3CH_2OH) can be formed from UV photolysis of condensed methanol.[20] All of these products except formic acid were observed in our studies following irradiation of condensed methanol with low-energy (≤ 20 eV) electrons. We attribute this difference to dissimilar experimental setups and procedures. The most conspicuous difference is the formation of methoxymethanol (CH_3OCH_2OH) via condensed-phase methanol reactions stimulated by low-energy electrons but not by UV photons. Resolution of this apparent difference between photon- and low-energy electron-induced reactions awaits additional photochemical studies of condensed methanol. Methoxymethanol could be a potential chemical tracer of the importance of low-energy electrons for the formation of complex organics in space if UV photolysis of methanol is shown not to produce methoxymethanol. However, the UV-induced formation of methoxymethanol from condensed methanol is likely given the detection of photolysis products formed from the methoxy ($CH_3O\bullet$) and hydroxymethyl ($\bullet CH_2OH$) radicals.

Conclusions

The similarity between the products of low-energy electron and UV-photon stimulated reactions of condensed methanol is suggestive of a potentially important contributing role for cosmic ray-induced, low-energy electrons in the synthesis of “complex” organic molecules in cosmic ices. If the low-energy electron- and UV photon-induced cross sections for the formation of two products is significantly different, the relative abundance of these products in the interstellar medium may provide insight into the relative importance of low-energy electrons vs. UV photons in the processing of cosmic ices. Such a comparison requires knowledge of the energy dependent electron flux whose calculation awaits Monte Carlo track simulations of cosmic ray particles traversing ices surrounding interstellar dust grains. These calculations must incorporate relativistic corrections given that galactic cosmic rays contain heavy ions of high charge and energy. While we cannot conclude with certainty that low-energy electrons contribute to the synthesis of molecules in space, it must be noted that low-energy electrons are the most abundant product of ionization radiation, such as cosmic rays, in condensed matter. However, based on what we know today, we cannot conclude with certainty whether the contributions of UV photons and low-energy electrons are equal, or if one dominates the other.

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