IR characterization and radiation chemistry of glycolaldehyde and ethylene glycol ices

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Abstract

Motivated by detections of glycolaldehyde and ethylene glycol in the interstellar medium and, for ethylene glycol, in comet Hale-Bopp, we report the low-temperature mid-IR spectra of these two molecules, including selected band strengths and positions. Each molecule has also been irradiated with 0.8 MeV protons to simulate cosmic-ray exposure, to measure each molecule's radiation lifetime, and to determine radiation chemical products. Evidence is presented that glycolaldehyde is readily formed from irradiated ethylene glycol ices, both in the presence and absence of H2O ice.

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1. Introduction

The reported number and complexity of organic molecules in comets and the interstellar medium (ISM) has continued to rise, raising new questions about molecular formation and stability. Although gas-phase chemical reactions are considered adequate to explain the presence of many organics, some molecules appear to require an active chemistry within icy mantles of interstellar grains. Exposure of ices at ~10 K to either cosmic radiation or far-UV photons can generate a variety of molecular species, which can then be ejected into the gas phase by various mechanisms (e.g. Bringa and Johnson, 2004, and references therein).

Two molecules which appear to require formation in ices are the recently-reported interstellar glycolaldehyde (Hollis et al., 2000) and ethylene glycol (Hollis et al., 2002). Fig. 1 shows the structure of each molecule. Since glycolaldehyde can be considered a sugar, with ethylene glycol as the corresponding hydrogenated alcohol, both of these species are astrobiologically relevant. Adding to this interest is the recent report of ethylene glycol in comet Hale-Bopp (Crovisier et al., 2004).

Although glycolaldehyde and ethylene glycol are two of the largest interstellar molecules, and ethylene glycol is currently the largest cometary molecule, their discoveries were not entirely surprising. Our laboratory experiments showed that proton-irradiated CH3OH formed ethylene glycol, leading us to predict that ethylene glycol is both a cometary and interstellar molecule (Hudson and Moore, 2000). Knowing that CH3OH dissociates into formaldehyde

\[ \text{CH}_3\text{OH} \rightarrow \text{H}_2\text{CO} \]

then the decomposition of ethylene glycol into glycolaldehyde

\[ \text{H}_2\text{C}_2\text{O}_2 \rightarrow \text{CH}_2\text{CHO} \]
HOCH₂CH₂OH → HOCH₂CHO

is expected. However, in contrast to the situation with CH₃OH and H₂CO, the astrochemical literature contains little on the characterization and chemistry of either solid-phase ethylene glycol or glycolaldehyde. Therefore, in this paper we present measurements of mid-IR spectra for these molecules at low temperatures (10 K), along with band positions and selected band strengths. We also report first experiments on the solid-phase radiation chemistry of each molecule in both the pure state and mixed with H₂O. These data will be needed to explore synthetic solid-phase pathways to glycolaldehyde and ethylene glycol, and to assess the radiation stability of each molecule.

2. Methods

Our experimental procedures are already in print, so only a summary is given here. Additional information can be found in Moore and Hudson (2003) and references therein.

Glycolaldehyde, hereafter denoted GA, was purchased as a dimer from Aldrich (Milwaukee, Wisconsin, USA), and heated under vacuum to about 80 °C to produce the gas-phase monomer. Amorphous ices containing GA were prepared by vapor-phase condensation of the monomer, or a mixture, onto a pre-cooled (10 K) aluminum substrate in a high-vacuum chamber. Ice thicknesses of several micrometers were reached in about 1 h, and were measured with a laser interference system. Intrinsic band strengths, denoted $A$ in cm mol⁻¹, were measured for GA using

$$A = \frac{\int \tau(\nu) \, d\nu}{N},$$

where $\int \tau(\nu) \, d\nu$ is an IR band’s integrated intensity (area) in cm⁻¹, and $N$ is the GA column density, $N$, in mol cm⁻².

The low vapor pressure of ethylene glycol, hereafter EG, prevented preparation of solid samples by vapor-phase condensation. Instead, ethylene glycol ices were made by slowly injecting the pure compound, or a (20:1) aqueous solution, onto a pre-cooled (10 K) substrate. The band strength of EG was determined by comparing the relative band intensities of EG and H₂O in the 1100–600 cm⁻¹ region for an injected H₂O+EG sample, assuming the H₂O:EG ratio to be the same in the ice as in the original injected solution, and then using the known band strengths of H₂O (Hudgins et al., 1993).

Infrared spectra of one-component and H₂O-dominated ices typically were recorded as 100- or 200-scan accumulations at a resolution of 4 cm⁻¹ from 5000 to 400 cm⁻¹, while experiments with Ar, N₂, and CO matrices were performed with 200-scan accumulations at 1 cm⁻¹ resolution. Spectra could be recorded at temperatures from about 8.8 to 300 K. For convenience, temperatures for spectra in the 8.8–10 K range are referred to simply as 10 K.

Ice samples were irradiated with 0.8 MeV protons from a Van de Graaff accelerator, with doses measured by counting the proton fluence (number of $p^+$/cm²) at the sample. All doses were converted to a common scale of eV/molecule as follows:

$$(\text{eV/molecule}) = (\text{fluence, in number of } p^+ / \text{cm}^2) \times (\text{stopping power of } 0.8 \text{ MeV } p^+) \times (\text{mass of a sample molecule, in grams}).$$

The radiation stopping powers and ranges used in our work were calculated with Ziegler’s SRIM program (Ziegler et al., 1985), and are summarized in Table 1, along with ice densities. Note that since sample thicknesses were on the order of a few micrometers, the bombarding protons penetrated the ices and came to rest in the underlying metal substrate, not in the ices themselves. See Moore et al. (2001) for details on the use of proton radiolysis to mimic cosmic ray bombardment.

![Fig. 1. Structures of glycolaldehyde and ethylene glycol molecules.](image-url)
3. Results

3.1. Glycolaldehyde spectra

Fig. 2 shows the mid-IR spectrum of amorphous GA at 10 and 150 K. Crystallization occurred in about 5 min at 165 K, so the spectra shown at 170 and 190 K are for crystalline material. Sublimation from the substrate was complete at 195 K after about 10 min. Several experiments were done on GA mixed with other materials, and Fig. 3 shows relevant spectra in the so-called IR fingerprint region. The spectrum with argon compares favorably with the results of Aspiala et al. (1986), but we are unaware of comparison spectra for other matrices. As expected, the GA features are much sharper in N₂, Ar, and CO at high dilution than in either pure GA or the H₂O mixture. Table 2 compares positions of the main GA features from 1800 to 600 cm⁻¹ for five different ices.

Table 3 lists band strengths, A values, for amorphous GA at 10 K. In some spectral regions, computing individual A values required curve fitting (Gaussian line shapes) to separate overlapping GA bands. Three absorbances in the 3708–2585 cm⁻¹ region are included in Table 3, although in ice experiments with H₂O those bands will be masked by water’s OH stretching features.

3.2. Ethylene glycol spectra

Fig. 4 shows spectra of amorphous EG and an H₂O + EG (20:1) mixture, both at 10 K. The EG features most easily seen in the H₂O-rich ice, and so most likely to be used in future experiments with H₂O mixtures, are the two absorbances in the 1100–1000 cm⁻¹ region. Curve fitting (Gaussian shapes) showed that these two EG bands were of almost equal intensity, within experimental error, and that their combined strength is \( A = 7.8 \times 10^{-18} \) cm mol⁻¹. Table 4 lists band positions for EG and H₂O + EG (20:1) ices in the 1500–500 cm⁻¹ region.

Crystallization of pure, amorphous EG occurred in about 30 min at 190 K, and sublimation of EG took place in about 20 min at 230 K. Our spectrum of crystalline EG is similar to that already published (Buckley and Giguère, 1967), and so is not shown here.

Experiments were not done with EG in inert matrices, such as argon, partly due to EG’s low volatility and...
partly because such experiments are already in print (Frei et al., 1977).

3.3. Radiation experiments

IR spectra of solid GA and EG were recorded before and after each molecule’s irradiation with 0.8 MeV protons. Fig. 5 shows the results for GA in the 2000–500 cm\(^{-1}\) region. About half of the GA molecules were destroyed by a radiation dose of 4.4 eV/molecule. All of the accompanying radiation products have not yet been identified, but features of the following (band positions in cm\(^{-1}\)), mostly seen on expansion of the spectra, are present: CO\(_2\) (2341, 657), CO (2134), H\(_2\)CO (1716, 1500), CH\(_4\) (1301), and, possibly, CH\(_3\)OH (1032). The absorbance growing at 1716 cm\(^{-1}\) is partly due to H\(_2\)CO, but a contribution from glyoxal, C\(_2\)H\(_2\)O\(_2\), is possible (Verderame et al., 1970).

Fig. 6 shows spectra for EG at 10 K before and after various radiation doses. Glycolaldehyde formation is shown by the rise of features at 1745 and 1374 cm\(^{-1}\), beginning with the smallest radiation dose. Other absorptions seen growing, most easily visible when the spectral scales are expanded, are for CO\(_2\) (2341, 657), CO (2134), H\(_2\)CO (1716, 1500), CH\(_4\) (1301), ethylene glycol (1040, 885?), and CH\(_3\)OH (1032). About half of the EG molecules were destroyed by a radiation dose of about 12.8 eV/molecule. A few experiments were performed with binary H\(_2\)O-rich ices, specifically H\(_2\)O + GA (18:1) and H\(_2\)O + EG (20:1). Radiation products in these experiments were much more difficult to identify than in the single-component ice experiments (Figs. 5 and 6), due to the broad bands of H\(_2\)O itself. For H\(_2\)O + GA (18:1), about half of the GA was destroyed with a radiation dose of only 0.2 eV/molecule, and the only products that could be identified with confidence were CO and CO\(_2\). In an H\(_2\)O + EG (20:1) ice, about half of the ethylene glycol was destroyed with a dose of about 1.2 eV/molecule. Growth of a weak absorbance at 1749 cm\(^{-1}\) was attrib-

### Table 4

<table>
<thead>
<tr>
<th>Pure EG</th>
<th>H(_2)O + EG (20:1)</th>
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<tbody>
<tr>
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<td>1046</td>
<td>1049(^a)</td>
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<tr>
<td>865</td>
<td>864</td>
</tr>
<tr>
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</tbody>
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\(^a\) Band strength \(A = 3.9 \times 10^{-18}\) cm mol\(^{-1}\).
uted to glycolaldehyde formation; other products observed were CO$_2$ (2341), CO (2134), and H$_2$CO (1714). These results, and those from pure GA EG ices, are summarized in Table 5.

Although our irradiations of EG produced GA, other syntheses also come to mind. Sodeau and Lee (1978) showed that GA is made by UV-induced dimerization of H$_2$CO trapped in solid argon.

\[
2\text{H}_2\text{CO} \rightarrow \text{H–C(=O)–CH}_2\text{OH (glycolaldehyde)}
\]

We will report on this reaction in the future. Another possible path to GA involves CO and CH$_3$OH, two known interstellar and cometary molecules. Since proton irradiation of CO + CH$_4$ ices produces acetaldehyde (Moore and Hudson, 2003, and references therein) according to

\[
\text{CO} + \text{CH}_4 \rightarrow \text{H–C(=O)–CH}_3 \quad \text{(acetaldehyde)}
\]

then proton irradiation of CO + CH$_3$OH might produce GA according to a similar reaction

\[
\text{CO} + \text{CH}_3\text{OH} \rightarrow \text{H–C(=O)–CH}_2\text{OH (glycolaldehyde)}
\]

Fig. 7 shows IR features of CO + CH$_3$OH (100:1) ice before and after irradiation to a dose of 1.1 eV/molecule at 20 K. Asterisks indicate weak features at the expected positions for GA, as documented by our reference spectra (Fig. 3) and band positions (Table 2).

4. Discussion

Our results form a basis for future work on the low-temperature chemistry of GA and EG, but a few points can already be made. First, the radiation half-lives of Table 5 show that GA is much more sensitive to radiation damage than EG, and that both molecules are more sensitive to destruction if H$_2$O is present. The formation of reactive species (H, OH, H$_2$O$^+$, e⁻) from H$_2$O evidently adds to the ways in which both GA and EG can be destroyed.

Another point concerns the relation of radiation doses in astronomical environments to those used in our work. Moore et al. (2001) give typical doses for selected environments within the Solar System and the interstellar medium. As an example, material within a cold, dense molecular cloud receives several eV/molecule during the cloud’s life ($10^6$–$10^7$ years). Taking a dose of 2 eV/molecule during $5 \times 10^6$ years, then over a million years a population of either solid-phase GA or EG molecules is preserved with little change in number. However, in the more likely case that GA or EG is surrounded by H$_2$O–ice, then the fraction of remaining molecules falls to about 25% and 80%, respectively.

As mentioned in Section 1, we and others have found that energetic processing of aliphatic alcohols produces aliphatic aldehydes, and vice versa. For example, interconversions of the one-carbon formaldehyde–methanol pair

\[
\text{HC(=O)H} \leftrightarrow \text{CH}_3\text{OH}
\]

and of the corresponding two-carbon pair

\[
\text{CH}_3\text{C(=O)H} \leftrightarrow \text{CH}_3\text{CH}_2\text{OH}
\]

have been studied in cosmic-ice analogs (e.g. Hudson and Moore, 2001; Allamandola et al., 1988). Similar reactions for the more complex GA and EG pair

\[
\text{HOCH}_2\text{C(=O)H} \leftrightarrow \text{HOCH}_2\text{CH}_2\text{OH}
\]
were anticipated and observed. This immediately suggests that if GA exists in interstellar or cometary ices, then the presence of EG can be expected. Our results also suggest that if EG is made in an ice, such as through dimerization of CH$_2$OH radicals from CH$_3$OH (Hudson and Moore, 2000), then GA should be present as well. Thus it is safe to predict that the ethylene glycol in comet Hale-Bopp (Crovisier et al., 2004) should be accompanied by glycolaldehyde. Assuming that EG is the precursor to GA, it should be possible to use our data to estimate an EG-to-GA ratio. Unfortunately this cannot be done until the rate of solid-phase production of EG is measured.

A third point concerns the energetic processing method used in our work, 0.8 MeV p$^+$ irradiation. The energy loss by incident MeV protons, and other ionizing radiations, is largely through ionizations and excitations in the eV range (Spinks and Woods, 1990). Therefore, we fully expect that experiments with X-rays, gamma rays, far-UV photons, and low-energy ions or electrons will show a chemistry similar to what we report.

Finally, the size of the molecules considered here, and the complexity of their chemistry, makes their IR study difficult. Chromatographic or mass spectrometric analyses of processed GA and EG are highly desirable to complement low-temperature work.

5. Summary and conclusions

Spectra of glycolaldehyde and ethylene glycol have been measured in both amorphous and crystalline states. Spectra were presented for H$_2$O-based, and other, mixtures, and selected IR intrinsic band strengths have been tabulated. Radiation chemical products of both GA and EG have been determined, showing that EG and GA readily convert into each other. Laboratory support is given for the synthesis of glycolaldehyde in irradiated H$_2$O + ethylene glycol and, more tentatively, apolar CO + CH$_3$OH ices. Based on this work we predict the presence of glycolaldehyde in comets.

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