Production of Complex Molecules in Astrophysical Ices

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Abstract. The inventory of interstellar and solar system molecules now numbers well over 100 species, including ions and molecules both charged and neutral. Gas-phase formation pathways for many of the observed organics are still uncertain, so that solid-phase syntheses are of interest. Low-temperature reactions are thought to occur within interstellar ices, on ice and grain surfaces in the interstellar medium, and on icy surfaces of solar system objects (e.g. Europa, Pluto). Ionizing radiation, such as cosmic rays, and far-UV photons are two possible initiators of such chemistry.

In the Cosmic Ice Lab at NASA's Goddard Space Flight Center, we can study both the photo- and radiation chemistries of ices at 8 - 300 K. Our most-recent work has been motivated by the detections of ethylene glycol, $HOCH_2CH_2OH$, in an interstellar source (Hollis, Lovas, Jewell, et al. 2002) and in comet Hale-Bopp (Crovisier, Bockelée-Morvan, Biver, et al. 2002). Ethylene glycol is currently the largest firmly-identified cometary molecule as well as one of the larger interstellar organics. This molecule's formation and accompanying chemistry provide challenges and tests for current astrochemical thought.

Here we discuss laboratory experiments on ethylene glycol's solid-phase formation and destruction. Using infrared spectroscopy, we have identified low-temperature radiation-chemical pathways that lead from known interstellar ices, such as either CH_3OH or H_2O and CO, to ethylene glycol. We also have identified a role for ethylene glycol in the formation of glycolaldehyde, $HOCH_2C(O)H$, a simple sugar (Hollis, Lovas & Jewell 2000). Related to these results are the 6- and 7-atom molecules formed by oxidation and reduction processes in irradiated H_2O + C_2H_2 ices. Analogous experiments have been conducted on two other triply-bonded molecules in H_2O-rich ice, HCN and N_2. An important focus of our work is the development of reaction schemes for the formation of complex molecules within astrochemically-relevant ices, and the use of such schemes to predict new molecules awaiting detection.

Keywords. astrobiology - astrochemistry - ISM: abundances - ISM: molecules - methods: laboratory - molecular processes

1. Introduction

The current inventory of interstellar (IS) and solar system molecules now numbers well over a hundred species including inorganics, organics, ions, and radicals. The most complex molecule has thirteen atoms. Of the stable organics, half can be considered nitrile and acetylene derivatives, with the other half being aldehydes, alcohols, ethers, acids, ketones, amides, and related molecules. Ethylene glycol, $HOCH_2CH_2OH$, is composed of ten atoms, and is the most complex organic identified in both comet Hale-Bopp (Crovisier et al. 2002) and IS environments (Hollis et al. 2000). Table 1 lists observed interstellar and circumstellar organic molecules, with cometary species indicated by underlining.

Table 1. Organic molecules observed in interstellar and circumstellar regions. A few related inorganic molecules are included.

Hydrocarbons and Simple Hydrides, Oxides, and Sulfides

CH_4	H_2O	NH_3	H_2S
C_2H_4	CO	N_2O	SO_2
C_2H_6	CO_2	N_2	OCS

Nitriles, Alkynes, and Related Molecules

CH_3CN	HCN	HNC	C_2H_2
$CH_3(CC)CN$	$H(CC)CN$	CH_3NC	$H(CC)_2H$
$CH_3(CC)_2CN$	$H(CC)_2CN$	$HCCNC$	$H(CC)_3H$
CH_2CHCN	$H(CC)_3CN$		$CH_3(CC)H$
CH_3CH_2CN	$H(CC)_4CN$	NH_2CN	$CH_3(CC)_2H$
	$H(CC)_5CN$		

Organics and Related Molecules

H_2CO	CH_3OH	$HCOOH$	CH_2CO
$HC(O)CH_3$	$CH_2CH(OH)$	CH_3COOH	
$H_3C\text{-}CH_2\text{-}C(O)H$	CH_3CH_2OH		$HNCO$
$H_2C=CH\text{-}C(O)H$	$HOCH_2CH_2OH$	$HC(O)OCH_3$	
$HCCH\text{-}C(O)H$			$HNCS$
$HOCH_2C(O)H$	$c\text{-}C_2H_4O$	$HC(O)NH_2$	H_2CS
	$(CH_3)_2O$	CH_2NH	CH_3SH
$(CH_3)_2CO$		CH_3NH_2	

Although a variety of astrochemical problems can be approached successfully through gas-phase chemistry, efficient syntheses for many interstellar and cometary organics are still unknown, so that solid-phase reactions are of interest. Among the gas-phase interstellar observations in which solid-phase chemistry has been invoked are those involving formaldehyde, H_2CO (Federmann & Allen 1991); methanol, CH_3OH (e.g. Charnley et al. 1995, Tielens & Whittet 1997, Teixeira et al. 1998); acetic acid, CH_3COOH (Mehringer et al. 1997); ethylene oxide, $c\text{-}C_2H_4O$ (Nummelin et al. 1998); methylenimene, CH_2NH (Dickens et al. 1997); ethyl cyanide, CH_3CH_2CN (Miao & Synder, 1997); vinyl alcohol, $CH_2CH(OH)$ (Turner & Apponi, 2001); ethylene glycol, $HOCH_2CH_2OH$ (Hollis et al. 2002); glycolaldehyde, $HOCH_2C(O)H$ (Hollis et al. 2000); and propenal, $CH_2CHC(O)H$, and propanal, $CH_3CH_2C(O)H$ (Hollis et al. 2004).

One way in which organics can be formed in space is through chemical reactions occurring within the icy mantles of interstellar grains. Reactions can be initiated by either particle radiation or high-energy photons, resulting in the synthesis of new molecular species which can then be ejected into the gas phase by various mechanisms (e.g. Bringa & Johnson, 2004, and references therein). Possible evidence for energetic processing within IS ices is the OCN^- ion (Hudson et al. 2001), while evidence for energetic processing in solar system ices comes from identifications of H_2O_2, O_2, and O_3 on Galilean moons. In comets, as with many interstellar regions, it is the many detections of gas-phase species that imply an active ice chemistry. In all cases, the importance of solid-phase reactions will depend on parameters such as initial ice composition, radiation flux, exposure time, temperature, and competing reactions.

Table 2 gives estimates of radiation and photon fluxes and doses for ices in both IS and solar system environments. Galactic cosmic rays are estimated to be about 87% protons,
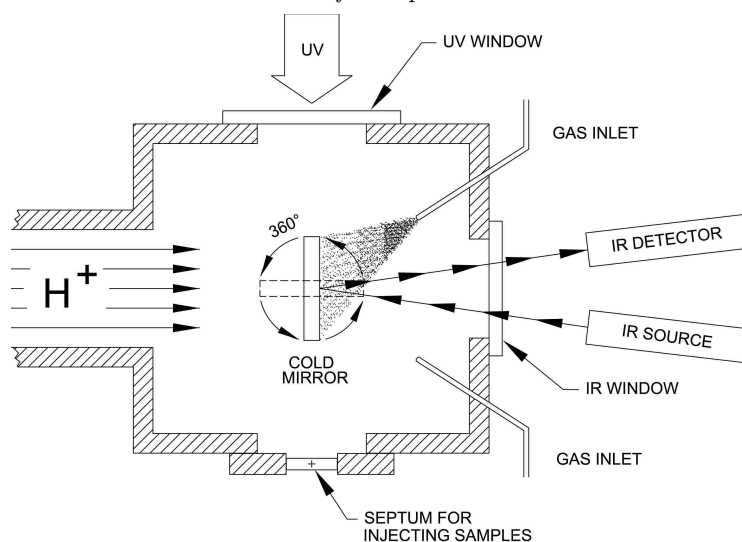
Figure 1. Schematic of laboratory set-up.

12% helium nuclei, and 1% heavier nuclei, with an overall isotropic flux assumed constant for the age of the solar system, $4.6{\times}10^9$ years. Since the IS electron cosmic-ray flux is 10-to-100 times smaller than the proton flux, for energies below 100 MeV the cosmic-ray processing of IS ices is dominated by protons. These protons have their greatest intensity in the low MeV range, and an energy spectrum decreasing with a power law index of 2.5 at higher energies. The estimated energy dose from impacting cosmic ray protons is $\sim$0.3 eV molecule^{-1} over 10^6 years, the approximate lifetime of a molecular cloud. Within this same time, $\sim$0.4 eV molecule^{-1} is deposited from UV photons that exist within dense cloud regions. Most of these IS photons are produced by hot O and B type stars, whose estimated abundance gives a calculated UV flux of $9.6{\times}10^8$ eV cm^{-2} s^{-1} between 91 and 180 nm.

The final products of photon- and radiation-induced chemical reactions within ices can be, and typically are, identical, but the processes by which the reaction products are made are quite different. The energy of a 1 MeV proton is deposited in an ice along a track containing numerous excitations and ionizations, with the concomitant production of thousands of secondary electrons causing most of the observed chemical changes. In contrast, each vacuum-UV photon is absorbed in a single excitation or ionization event. For comparison, in a 1 g cm^{-3} H$_2$O-ice the range of a 1 MeV proton is $\sim$20 μm, while there is a 37% drop in UV transmission in 0.15 μm, assuming a UV cross-section of $2{\times}10^{-18}$ cm^2 (Okabe 1978).

In our laboratory we synthesize complex organic molecules in cosmic-ice analogs, with reactions initiated by either high-energy protons ($\sim$1 MeV), to mimic cosmic rays, or vacuum-UV photons. We systematically vary reaction doses, temperatures, abundances of both minor and major (matrix) materials, and overall sample size (ice thickness). We also routinely employ isotopic labeling and isoelectronic systems to identify reaction products and test promising mechanisms. This approach allows us to understand and predict new interstellar molecules, and to identify processes and products that less comprehensive strategies would miss.

For this paper we describe the synthesis of complex organics from three triply-bonded molecules: carbon monoxide (C$\equiv$O), acetylene (HC$\equiv$CH), and hydrogen cyanide (HC$\equiv$N). These unsaturated, isoelectronic, linear molecules are all highly-reactive, and all are de-

Table 2. Estimated UV photon and 1 MeV proton fluxes in different regions of space, and doses experienced by ices.

Region	Residence Time of Ices in Region (years)	UV[a]		Cosmic Ray Protons[a]	
		Flux 10 eV photon eV cm^{-2}s^{-1}	Energy Dose eV molecule^{-1}	Flux 1 MeV proton eV cm^{-2}s^{-1}	Energy Dose eV molecule^{-1}
IS Cold Dense Cloud (0.02 μm ice)	10^6 10^7	1.4×10^4	0.4 4	1×10^6	0.3 3
Oort Cloud and KBO Region	4.6×10^9	9.6×10^8	10^8 (top 0.015 μm layer)	Energy dependent flux $\phi(E)$	150 (0.1 m) 55-5 (1-5 m)
Jovian Satellites e.g. Europa[b]	$<1\times10^8$	4×10^{13}	10^{13} (top 0.015 μm layer)	Magnetospheric ions 7.8×10^{13}	150 (1 cm 10^4 years)
Typical Lab Experiment	4.6×10^{-4}	8.6×10^{14}	14	7×10^{10}	9

[a]Energy dose for UV and cosmic ray protons for the IS medium is from Moore et al. (2001), for the Oort cloud, KBO and Jovian satellite regions from Moore et al. (2003) and references therein. [b]Possible resurfacing lifetime from Stern and McKinnon (2000).

tected in both IS and solar system environments. These three species are the starting point for making about twenty different molecules, radicals, and ions where, for CO and C_2H_2, the primary syntheses are based on reactions of H and OH radicals; for HCN the primary observed reaction path is oxidation of the cyano (-CN) functional group. Here we highlight radiation experiments in which we have identified the infrared (IR) signatures of complex species in H_2O-rich ices containing CO, C_2H_2, or HCN. Since actual cosmic ices are not simple binary systems, we have also had to consider the roles played by other molecules and reactions, such as the formation of ions through acid-base chemistry with NH_3. Finally, our results for these simple systems permit predictions of yet undetected, and more complex, organic molecules in comets and IS space.

2. Laboratory Methods

Details of our experimental set-up, ice preparation, IR spectral measurements, cryostat, and proton beam source have been published (Moore & Hudson 2000; Moore & Hudson, 1998). Figure 1 is a schematic that represents an ice sample within our sample chamber. Briefly, ices were formed by condensation of gas-phase mixtures onto a precooled aluminum mirror at 10 - 20 K, where mid-IR spectra (4000 - 400 cm^{-1}) of ices were taken by reflection from the mirror. Ices were 1 - 5 μm thick, as determined by a laser interference fringe system. Samples temperatures were controlled from 10 to 300 K with a heater on the cryostat tail section.

IR spectra were recorded before and after exposure of ice samples to a 0.8 MeV proton beam from a Van de Graaff accelerator. The use of proton irradiation to simulate cosmic-ray bombardment has been discussed earlier (e.g. Hudson & Moore, 2001; Moore et al. 1983). Since sample ice thicknesses were less than the range of the incident 0.8 MeV protons, the bombarding ions penetrated the ices and came to rest in the underlying metal substrate, not in the ices themselves. Radiation doses were determined by counting the proton fluence (p^+ cm^{-2}) at the ice, and converting to a common scale of eV (18-amu molecule)$^{-1}$. Proton stopping powers and ranges were calculated with Ziegler's SRIM program (Ziegler et al. 1985; www.srim.org).

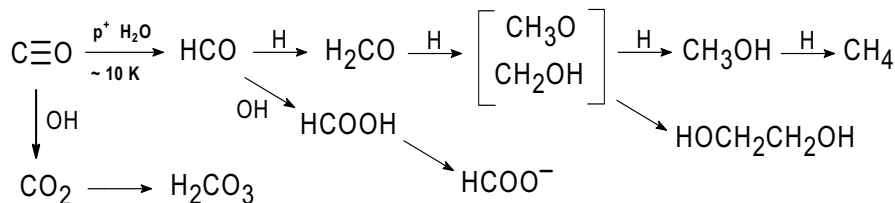## 3. Laboratory Studies of Unsaturated Carbon-Containing Species in H_2O-Rich Ices

3.1. *Study of CO in H_2O Ice*

To make a complex organic molecule, a laboratory chemist selects a simpler starting material and performs reactions such as those of addition or substitution of atoms or functional groups. In cometary and IS ices, carbon monoxide trails only H_2O in abundance, and so is a likely source of solid-phase organic chemistry. The H_2O-ice itself, subject to ionizing radiation, is a ready source of H atoms, OH radicals, H_2O^+, and e^-. These reactive species are available to participate in reactions such as H_2O_2 formation, protonation by H_2O^+ (or H_3O^+), OH radical addition, and reduction by e^-. The possibility that such chemistry might take place in astronomical ices is at least 10 years old (Tielens & Allamandola 1987; Mumma et al. 1996), and probably much older.
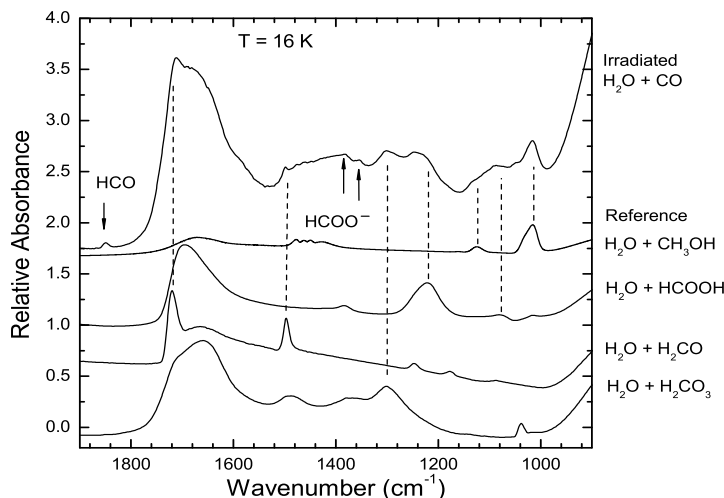
Reaction Scheme 1 summarizes the first laboratory irradiations of H_2O + CO ices (Hudson & Moore 1999), where brackets indicate presumed but unobserved products. Radiation processing of H_2O + CO mixtures formed HCO, H_2CO, and CH_3OH through H-addition, and formic acid (HCOOH) in a branching reaction step. In addition, CO_2 was efficiently made by O-atom transfer from OH radicals to CO. Figure 2 shows the IR spectrum, in the 1900 - 1000 cm^{-1} region, of an H_2O + CO (5:1) ice after irradiation to 11 eV molecule^{-1} at 16 K. Bands of H_2CO, CH_3OH, and HCOOH in this region are identified by comparison with reference spectra of dilute mixtures of each of molecule in H_2O-ice. The HCO radical is at 1853 cm^{-1}. Similar experiments were performed at other H_2O/CO ratios (Hudson & Moore 1999) and in the presence of NH_3 (Hudson et al. 2001).

One of the most important findings from these experiments was the relatively high percentage of conversion of CO into other molecules. After about 22 eV molecule^{-1}, for an ice whose initial H_2O/CO ratio was 5, the conversion of CO into CO_2 was ∼20%, HCOOH ∼40%, H_2CO ∼7% and CH_3OH ∼9%. These percentages are a function of the initial CO abundance and the radiation dose. They are calculated by knowing integrated band strengths of each molecule and assuming an ice density (Hudson & Moore 1999 for details).

A comparison of our results with hydrogenation experiments of Watanabe et al. (2003, 2004) is shown in Figure 3. In their experiments, the source of H atoms was a cold atomic hydrogen beam simulating the emplacement of H-atoms onto IS ice grain mantles in cold dark clouds. Hydrogenation of H_2O + CO (4:1) ices resulted in production of both H_2CO and CH_3OH. Watanabe et al. (2003, 2004) assumed a 10^4 - 10^6 year exposure to an H-atom density of 1 cm^{-3} at 10 K. Ratios of column densities of CO/CH_3OH and H_2CO/CH_3OH are plotted in Figure 3. The left-hand data point is equivalent to 10^6 years, and the right-hand data point to 10^4 years (based on Watanabe et al. 2004, Figure

$$C\equiv O \xrightarrow[\sim 10\,K]{p^+\ H_2O} HCO \xrightarrow{H} H_2CO \xrightarrow{H} \begin{bmatrix} CH_3O \\ CH_2OH \end{bmatrix} \xrightarrow{H} CH_3OH \xrightarrow{H} CH_4$$

HCO → (OH) → HCOOH

CH₃O/CH₂OH → HOCH₂CH₂OH

$CO \xrightarrow{OH} CO_2 \longrightarrow H_2CO_3$

HCOOH → HCOO⁻

REACTION SCHEME 1

Figure 2. New species formed in an H_2O + CO (5:1) ice irradiated to 11 eV molecule^{-1} are identified by comparison with reference spectra of dilute mixtures of organics at $\sim$16 K. Spectra are offset for clarity.

5). Our results are plotted to show data representing exposure of an H_2O + CO (5:1) ice to $\sim$1, 10, and 22 eV molecule^{-1} corresponding to cosmic-ray proton exposure for 3×10^6, 3×10^7, and 7×10^7 years in a dense 10 K cloud. Both types of experiments appear able to convert CO to H_2CO and CH_3OH at levels comparable to those detected in cometary comae and interstellar ices. Note, however, that the rate of conversion of CO by H atoms is still controversial (Hiraoka et al. 2002, 2005).

3.1.1. *CH_3OH as a Starting Point for Ethylene Glycol Formation*

Once formed, CH_3OH can undergo other reactions to make more complex molecules. Results from our experiments on H_2O + CH_3OH ice (3:1) showed that after irradiation at 16 K, CO, CO_2, HCO, H_2CO, $HCOO^-$, and ethylene glycol ($HOCH_2CH_2OH$) are present (Hudson & Moore, 2000a). Figure 4 shows the sample's IR spectra before and after irradiation. Absorptions at 1088 cm^{-1} (peak) and 1046 cm^{-1} (shoulder) are matched with a reference spectrum of ethylene glycol. This molecule's formation is explained by straightforward reaction chemistry in which hydroxymethyl radicals (CH_2OH), produced by proton irradiation of CH_3OH, couple to make $HOCH_2CH_2OH$ (schematically shown in Scheme 1).
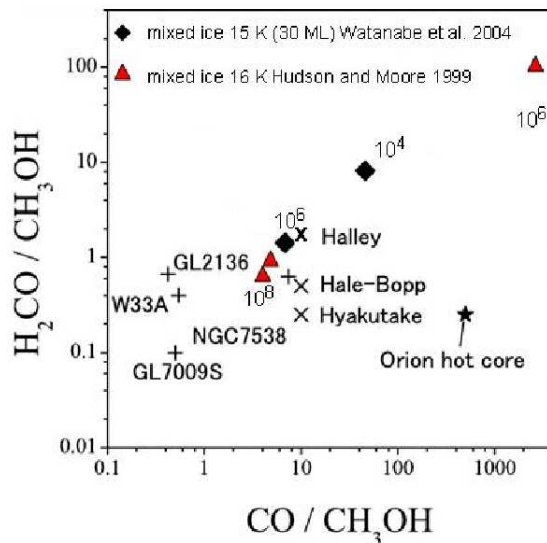
Figure 3. Abundance ratios of H_2CO and CO, relative to CH_3OH, are compared for hydrogenation results of Watanabe et al. (2004) on H_2O+CO (4:1) ice at 15 K, proton irradiation results of Hudson & Moore (1999) on $H_2O + CO$ (5:1) ice at $\sim$16 K, and observed ratios in interstellar ices, comets, and the Orion hot core. The graph is based on Watanabe et al. (2004, Fig. 5), and shows increasing processing from right to left. Powers of 10 indicate the ice's estimated exposure time (in years) to either the H fluence in molecular clouds (Watanabe's data) or the 1-MeV H^+ cosmic-ray fluence (Hudson's data).

3.1.2. *Relationship Between Ethylene Glycol and Glycolaldehyde*

Recently we reported the solid-phase synthesis of glycolaldehyde ($HOCH_2C(O)H$) in irradiated ices containing ethylene glycol, both with and without H_2O (Hudson et al. 2005). This reaction is consistent with other aldehyde-alcohol interconversions which we have studied, such as for the pairs [H_2CO, CH_3OH] and [$CH_3C(O)H$, CH_3CH_2OH] (Hudson & Moore, 2001). Figure 5 shows the changes in the IR spectrum of ethylene glycol ice during proton irradiation.

Another route we examined for glycolaldehyde formation will apply when CH_3OH exists in a CO-rich (apolar) ice. Figure 6 shows the IR spectrum of CO + CH_3OH (100:1) after radiolysis. In this ice, rupture of a CH bond gives an H atom that reacts with the CO matrix to make HCO, with a subsequent radical-radical reaction between HCO and CH_2OH giving glycolaldehyde. Two weak features in Figure 6 indicate the presence of $HOCH_2C(O)H$, as shown by our reference spectrum. Other products include the HCO radical, H_2CO, and $CH_3C(O)H$.

3.2. *Study of C_2H_2 in H_2O Ices*

A second small, carbon-containing, unsaturated molecule we examined is acetylene (C_2H_2). Acetylene forms in the photospheres of AGB stars where C/O$\gg$1, locking up most of the elemental carbon. Gas-phase acetylene and its derivatives are thought to be the building bocks of PAHs and soot (e.g. Tielens & Charnley 1997). When C_2H_2 is condensed into an icy grain mantle, however, H-atom addition reactions are possible, resulting in C_2H_6 (Charnley et al. 1992, 1995). In fact, it was the detection of nearly equal abundances of C_2H_6, C_2H_2, and CH_4 in Comets C/1996 B2 Hyakutake and C/1996 O1 Hale-Bopp that led Mumma et al. (1996) to point out that these cometary species did not origi-
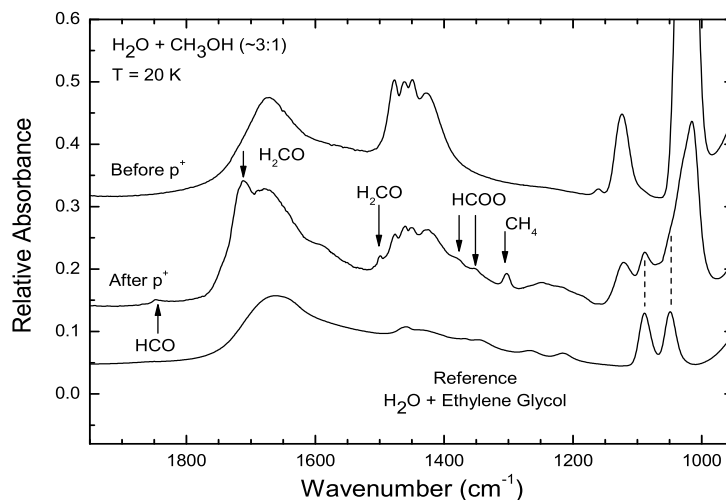
Figure 4. IR spectra of H_2O + CH_3OH ice before (upper) and after (middle) an irradiation to ~18 eV molecule^{-1} with 0.8 MeV protons. New products include H_2CO, CH_4, $HCOO^-$, and ethylene glycol. At the bottom is a spectrum of unirradiated H_2O + ethylene glycol for reference. Not shown are several other confirming bands for ethylene glycol between 500 and 1000 cm^{-1}.
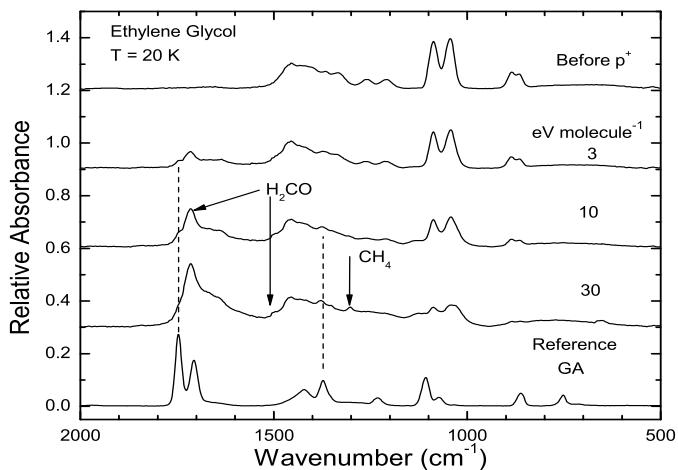

Figure 5. IR spectra of ethylene glycol before and after proton irradiation to a dose of ~3, 10, and 30 eV molecule^{-1} compared to a spectrum of glycolaldehyde (GA) at 20 K.

nate in a thermochemically-equilibrated region of the solar nebula. Instead, the observed abundances were consistent with expected production of C_2H_6 in interstellar icy grain mantles. Similar abundances for these organic volatiles were also found in Comet Lee, 153P/Ikeya-Zhang, and 9P/Tempel-1 (post-impact). See Mumma et al. (2005) and references therein.
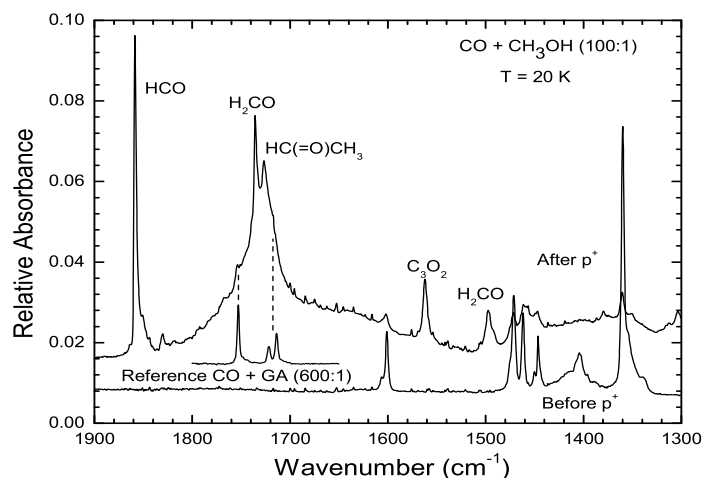
Figure 6. IR spectra of CO + CH$_3$OH (100:1) before (lower) and after (upper) irradiation with 0.8 MeV protons to a dose of $\sim$1 eV molecule^{-1}. A reference spectrum of CO + glycolaldehyde (GA) (600:1) is compared with weak features on the wings of the large 1730 cm^{-1} band.
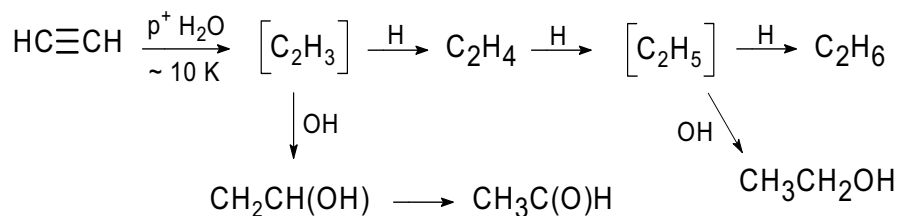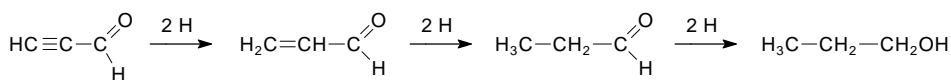

REACTION SCHEME 2

We have shown experimentally that radiation processing of H$_2$O + C$_2$H$_2$ ices forms C$_2$H$_4$ and C$_2$H$_6$ through H addition (Moore & Hudson 1998) in the condensed phase. CH$_3$C(O)H, C$_2$H$_6$, CH$_2$CH(OH), and C$_2$H$_5$OH form through the multi-step reactions seen in Reaction Scheme 2. In addition, both CO$_2$ and CO are detected along with H$_2$CO. Figure 7 shows IR spectra of H$_2$O + C$_2$H$_2$ (4:1) at 20 K before and after a dose of 17 eV molecule^{-1}. Additional C$_2$H$_6$ absorptions at 2880, 2939, and 2975 cm^{-1} were stronger than the weak 1464 cm^{-1} band shown in this region, and aided in the spectral assignments. The identifications of the isomers vinyl alcohol and acetaldehyde, CH$_2$CH(OH) and CH$_3$C(O)H respectively, are especially interesting (Hudson & Moore, 2003) as both are known interstellar molecules. Our experiments support the idea that a similar chemistry produces these molecules in interstellar space.

The abundance ratios of CH$_4$, C$_2$H$_6$, and C$_2$H$_2$ in these experiments are sufficient to explain the cometary observations. Variables that did change the final abundances include the radiation dose, the dilution of C$_2$H$_2$ in the starting ice, and the initial presence of CH$_4$ in the ice. Since we did not observe C$_2$H$_2$ formation in irradiated H$_2$O + CH$_4$ mixtures, but did find CH$_4$ formation in H$_2$O + C$_2$H$_2$ ices, we conclude that relevant
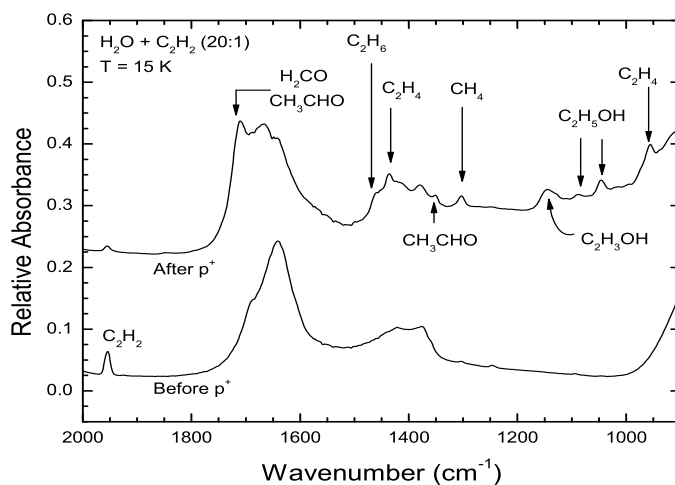
Figure 7. IR spectra of $H_2O + C_2H_2$ before and after irradiation to a dose of 17 eV molecule^{-1}. New products are identified by comparison with appropriate reference spectra (see Moore & Hudson 1998).
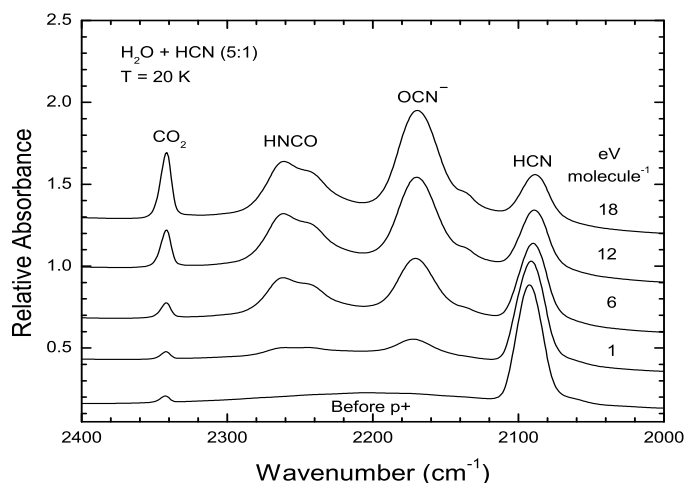

REACTION SCHEME 3

hydrocarbon chemistry for these comets is founded on H addition to C_2H_2, as opposed to CH_4 reactions. This suggests that C_2H_2 is part of the natal cometary ice composition.

Extrapolating these results to a more complex molecule, propynal ($HC\equiv CC(O)H$), similar H-addition reactions are expected to form propenal and propanal. All three of these aldehydes have been observed in Sagittarius B2(N) (Hollis et al. 2004). The H-atom addition sequence connecting these molecules is expected to be that shown in Reaction Scheme 3. Although only the first three organics in Reaction Scheme 3 have been identified as interstellar, the conversion of aldehydes to alcohols is consistently found in our experiments. Therefore, we safely predict the conversion of propanal into n-propanol, and encourage observational searches for the latter.

3.3. *Study of HCN in H_2O Ices*

A third unsaturated, carbon-containing molecule we examined is HCN. This molecule is seen in the gas phase in the interstellar medium (e.g. Snyder & Buhl, 1971; Boonman et al. 2001) and in cometary comae (e.g. Ip et al. 1990; Bockelée-Morvan et al. 1994; Magee-Sauer et al. 1999). It is also thought that HCN is a native nuclear ice component in comets. The idea that HCN might participate in the chemistry of interstellar ice mantles was the motivation for our experiments on H_2O + HCN ices (Gerakines et al. 2004).

Solid-phase HCN reactions analogous to those with CO and C_2H_2 will result in methylen-imine (CH_2NH) and methylamine (CH_3NH_2), both being IS gas-phase molecules. However, our experiments showed that oxidation products of HCN dominated the IR spectrum of H_2O + HCN ices after radiolysis. Figure 8 shows the 2400 - 2000 cm^{-1} region

Figure 8. IR spectra of H_2O + HCN before and after irradiation to a dose of $\sim$1, 6, 12, and 18 eV molecule^{-1}. New products include HNCO, OCN$^-$, and CO_2.
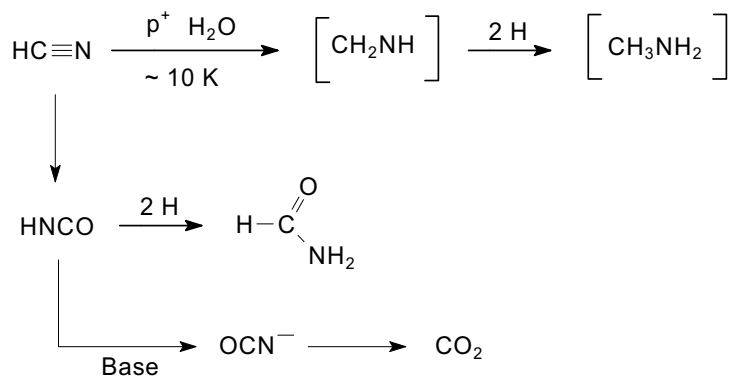
REACTION SCHEME 4

for H_2O + HCN (5:1) at 18 K before and after several radiation doses (Gerakines et al. 2004). Identified products are the cyanate anion (OCN$^-$), isocyanic acid (HNCO), and CO_2. Features in the 1800 - 1000 cm^{-1} region (not shown) were identified with the NH_4^+ cation at 1470 cm^{-1} and formamide (HCONH$_2$) at both 1686 and 1386 cm^{-1}. Steps leading to these products are shown in Reaction Scheme 4.

Although IS ices are dominated by H_2O, and neither HCN nor any organic nitrile has been identified in them, these ices often show an intense IR feature due to OCN$^-$ (Hudson et al. 2001). This observation of OCN$^-$, as opposed to HCN and nitriles, can be understood from our experiments, since our work demonstrates the ease with which OCN$^-$ forms in H_2O + HCN mixtures. Morover, HCN is not the only possible source of cyanate, as subsequent irradiations of many nitriles in H_2O-ice all showed OCN$^-$ formation (Hudson & Moore 2004). This suggests that the cyanate ion may be a marker for energetic processing. Like CO_2, the cyanate ion is a stable, linear, 16-electron species.

It has been seen in warming experiments to $\sim$200 K (Moore & Hudson 2003), and is predicted to be on the surfaces of outer solar system bodies.

HNCO, indicated in Figure 8, is detected only as a gas-phase species in both interstellar sources and comets (e.g. Gibb et al. 2000; Schutte & Khanna 2003 and references therein). Its absence in IS ices suggests that it reacts to form OCN^- and a counter-ion. Candidate bases include H_2O, formamide, and methylamine. More likely, HNCO combines with NH_3 to make OCN^- and NH_4^+. In fact, features in several interstellar sources are attributed to NH_4^+ (Schutte & Khanna, 2003).

4. Conclusions

Our experiments demonstrate that several types of chemical reactions are involved in making complex molecules. In irradiated H_2O-rich ices containing CO or C_2H_2, H- and OH- additions produce many stable organics, some more oxidized than the reactants, and some more reduced. Radicals formed during irradiation can dimerize, thereby lengthening carbon chains. Examples include the dimerization of CH_3 to form C_2H_6 (Moore & Hudson 1998) and, more recently, the dimerization of CH_2OH to make $HOCH_2CH_2OH$ (Hudson et al. 2005). Current experiments involve studies of 2 $CH_2CN \rightarrow (CH_2CN)_2$ in processed H_2O + CH_3CN. This is work in progress and relies on HPLC analysis of irradiated ice residues. It shows that identification of complex molecules are often at the limit of IR capabilities and require more-sensitive analytical techniques.

We have also found isomerization reactions to help explain the presence of isomeric pairs such as vinyl alcohol and acetaldehyde. Our work shows that vinyl alcohol is made in irradiated H_2O + C_2H_2, and then isomerizes to acetaldehyde. Among the nitriles, isomerizations include $HCN \rightarrow HNC$ and $CH_3CN \rightarrow CH_3NC$ (Hudson & Moore 2004), and formation of ketenimines such as $CH_3CN \rightarrow H_2C{=}C{=}NH$. Extensions give a prediction of interstellar carbodiimide from cyanamide ($NH_2C{\equiv}N \rightarrow HN{=}C{=}NH$) and allene from methylacetylene ($CH_3C{\equiv}CH \rightarrow H_2C{=}C{=}CH_2$).

Interconversions of aldehydes and alcohols are examples of both H-atom addition and the reverse reaction (hydrogen elimination). Our work has included the following: [H_2CO, CH_3OH], [$CH_3C(O)H$, CH_3CH_2OH], and [$HOCH_2C(O)H$, $HOCH_2CH_2OH$]. This chemistry is expected to apply to more-complex pairs such as [$HC{\equiv}C{-}C(O)H$, $HC{\equiv}C{-}CH_2OH$], [$H_2C{=}CH{-}C(O)H$, $H_2C{=}CH{-}CH_2OH$], and [$H_3C{-}CH_2{-}C(O)H$, $H_3C{-}CH_2{-}CH_2OH$]. Therefore, our experiments suggest that IS aldehyde-alcohol pairs are likely if either member participates in condensed-phase radiation chemistry.

In all cases, formation paths compete with dissociation and elimination processes that lead to less-complex molecules. Acid-base reactions can also play a role, particularly regarding the formation of ions. Altogether, the reactions examined lead to about 50% of the known stable IS organics containing oxygen, and most of those found in comets. These observations show that discovering the identities of and reactions paths for complex interstellar molecules will require a firm understanding of simpler systems.

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Discussion