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Laboratory Studies of the Formation of Methanol and Other Organic Molecules by Water + Carbon Monoxide Radiolysis: Relevance to Comets, Icy Satellites, and Interstellar Ices

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Radiation processing of cometary, planetary, and interstellar ices has been investigated by irradiating mixtures of H_2O and CO near 16 K with 0.8-MeV protons. IR spectroscopy and isotopic substitution showed that H and OH, from H_2O, added to CO to form HCO, H_2CO, HCOOH, and CH_3OH. *A* values (integrated spectral absorbances) for HCOOH and HCO trapped in H_2O ice were measured for the first time. These new values, along with published *A*'s for H_2CO and CH_3OH, were used to calculate radiation yields (*G* values) and conventional percentage yields. Significantly higher percentage yields of HCOOH and CH_3OH were observed, compared to previous solid-state H_2O + CO experiments. This suggests that radiation processing may help explain the discrepancy between the observed gas-phase abundances of small organic molecules and the abundances predicted by current theoretical models and previous laboratory experiments. In contrast to previous experiments on one-component ices, no spectral evidence for long-chain molecules was found in the present work. This demonstrates that ice composition is a critical factor in applying laboratory results to cometary, icy satellite, and interstellar ices.

Key Words: **ices; comets; composition; radiation chemistry; organic chemistry; spectroscopy.**

INTRODUCTION AND BACKGROUND

The standard picture of cometary formation involves accretion of interstellar grains into icy macroscopic bodies. These grains are exposed to ionizing radiation in several distinct time periods, starting with exposure to cosmic and UV radiation prior to accretion. Much later, the surface ices of a comet experience additional radiation exposure from cosmic rays while in the Oort cloud for 4.6 billion years. All of these irradiations alter the chemical and physical properties of both interstellar and cometary ices, synthesizing new molecules and destroying others. Thus the molecules observed during a comet's passage through the Solar System are the result of, among other things, the irradiation of an icy material at low temperatures.

Comet Hyakutake provides an example of how such solid-phase irradiation can be important. Ethane (C_2H_6) and methane (CH_4) were observed in Hyakutake with abundances much higher than expected from gas-phase models (Mumma *et al.* 1996). It was suggested (Mumma *et al.* 1996) that the C_2H_6 abundance was due to solid-phase H-atom addition to acetylene (C_2H_2), although few, if any, supporting experiments were available. Our own laboratory investigations subsequently showed that proton irradiation of amorphous $H_2O + C_2H_2$ ices at ~15 K indeed results in H-atom addition to C_2H_2 to form C_2H_6 (Hudson and Moore 1997, Moore and Hudson 1998).

Low-temperature solid-phase reactions are of considerable interest beyond the case of hydrocarbons. While gas-phase models have enjoyed some success in predicting interstellar molecular abundances, solid-phase reactions on and in ice-dust grains have been linked to many observations. Among the *gas-phase* interstellar observations in which solid-phase chemistry has been invoked are those involving formaldehyde, H_2CO (Federman and Allen 1991), acetic acid, CH_3COOH (Mehringer *et al.* 1997), ethylene oxide, c-C_2H_4O (Nummelin *et al.* 1998), methylenimene, CH_2NH (Dickens *et al.* 1997), and ethyl cyanide, CH_3CH_2CN, (Miao and Synder 1997). Methanol (CH_3OH) is another molecule of interest in both comets and the interstellar medium (ISM). Its production has been investigated by several groups, the conclusion being that grain chemistry is needed to explain the observed gas-phase CH_3OH abundances (e.g., Charnley *et al.* 1995, Tielens and Whittet 1997, Teixeira *et al.* 1998).

In Table I we summarize the abundances of CH_3OH and other molecules in ices of an interstellar object studied with the

TABLE I
Molecular Abundances in Comets and Interstellar Ices

Molecule	Cometary volatiles Hyakutake[a]	Cometary volatiles Hale–Bopp[b]	Interstellar ices IRS-9[d]
H_2O	=100	=100	=100
CO	5–30	20	15
CO_2	<7	6	12
CH_3OH	2	2	6.3
H_2CO	0.2–1	1	<3 tentative
HCOOH		0.05	3 tentative
CH_4	0.7	~1	1.6
C_2H_2	0.3–0.9	~0.5[c]	
C_2H_6	0.4	~0.5[c]	
NH_3	0.5	0.6	<6
x-CN	0.01	0.37	0.5
OCS, XCS	0.3	0.7	
SO_2		0.15	

[a] Bockelee-Morvan (1997).
[b] Crovisier (1998).
[c] Campins (1998).
[d] Schutte (1999).

Infrared Space Observatory (ISO) and in the comae of two recent comets. After H_2O, carbon monoxide (CO) leads in abudance in all three objects and probably accounts for the fact that carbon dioxide (CO_2) is third highest in abundance for all three objects listed. Specifically, reactions of CO can generated carbon dioxide by either UV (Allamandola *et al*. 1988) or cosmic ray (Moore *et al*. 1991) processing of ice grains. Continuing down each column of Table I, CO also has often been considered as a source for the two next-most-abundant molecules, H_2CO and CH_3OH. A likely reaction sequence leading from CO to H_2CO and then to CH_3OH is

$$CO \rightarrow HCO \rightarrow H_2CO \rightarrow CH_3O \text{ and } CH_2OH \rightarrow CH_3OH.$$

Charnley *et al*. (1997), Tielens and Whittet (1997), Kaiser *et al*. (1997), Delitsky and Lane (1998), and Schutte *et al*. (1996a) have all pointed out that H-atom addition to CO in and on icy interstellar grain mantles, cometary surfaces, and planetary satellites might well be a source of more complex molecules, such as H_2CO and CH_3OH. Accreted H atoms could be responsible for reducing CO to CH_3OH on a grain surface or, alternatively, H atoms could be produced by ionizing radiation or UV photons acting on a polar grain mantle, for example, one dominated by H_2O.

Given the possible importance of the low-temperature, solid-phase reaction sequence $CO \rightarrow H_2CO \rightarrow CH_3OH$, extensive laboratory studies of these reactions are expected. Therefore, it is surprising that *very* few spectroscopic studies of these reactions are found in the standard refereed journals. In the specific case of interest to us, CO chemistry in H_2O-dominated ices, the literature is extremely sparse. Allamandola *et al*. (1988) UV-photolyzed a $H_2O : CO = 20 : 1$ mixture and observed HCO, H_2CO, and CO_2 as "weak bands" in IR spectra. Other reports on these conversions have involved much higher initial CO abundances, so that the ice mixture's polarity is greatly reduced, or they have involved three-component (or more complex) mixtures, so that the underlying reaction chemistry is masked. Even in photolysis experiments in which the initial CO concentration was high, the conversion of CO to H_2CO was only on the order of "a few percent" and, for a separate experiment, the conversion of H_2CO to CH_3OH was called "quite inefficient" (Schutte *et al*. 1996a). In a different type of experiment, Hiraoka *et al*. (1998) sprayed H atoms, formed by electrical discharge of H_2, onto frozen CO at 12 K. On warming the sample to ~100 K, they observed the release of H_2CO and CH_3OH with mass spectrometry, but with calculated conversions from CO of only 0.012 and 0.003%, respectively. In short, so far neither photolysis nor discharge experiments have uncovered a promising path from CO to H_2CO and CH_3OH. No relevant $H_2O + CO$ ion irradiation experiments have been published.

We now have extended our H-atom addition experiments from C_2H_2 to CO, an abundant cometary and interstellar molecule. In this paper we show that CO is hydrogenated by ion irradiation at low temperatures in amorphous water, conditions under which cometary and interstellar CO exists. We demonstrate that radiation reduces CO first to H_2CO and then to CH_3OH and that CO also produces formic acid (HCOOH). Finally, we show that irradiation of $H_2O + CO$ ices gives higher conversions to reduced products than do either UV photolysis or electrical discharge experiments.

EXPERIMENTAL

Figure 1 shows our experimental arrangement. Solid samples, called simply "ices," were prepared by slow condensation from appropriate vapor-phase mixtures at room temperature onto a polished aluminum disk (area ≈ 5 cm^2) held near 16 K in a vacuum chamber. A Fourier-transform infrared (FTIR) spectrometer then recorded the spectrum of the frozen solid in the region of interest, usually 400–4000 cm^{-1}. Next, the sample was rotated to face a 0.8-MeV proton beam from a Van de Graaff accelerator, irradiated to the desired dose, and then rotated back to face the spectrometer where its IR spectrum was recorded a second time. Additional irradiations could be performed as desired with spectra taken after each. These single-beam spectra were ratioed against the spectrum of the blank aluminum substrate to get a transmission-type spectrum which could be converted into an absorbance spectrum. Spectra usually were recorded as 60-scan accumulations at a resolution of 4 cm^{-1}.

The sources and purities of gases and liquids used in these experiments follow: triply distilled H_2O with a resistance greater than 10^7 ohm cm; CO, Matheson research grade, 99.99%; $C^{18}O$, Miles Laboratories, 90.83% ^{18}O; CH_3OH, Sigma–Aldrich HPLC grade, 99.9%; H_2CO, Fisher, purified trioxymethylene; HCOOH, Fisher Scientific, 99.9%; C_2H_2, Matheson, was purified using a slush bath at 173 K; CH_4, Matheson research grade, 99.999%.

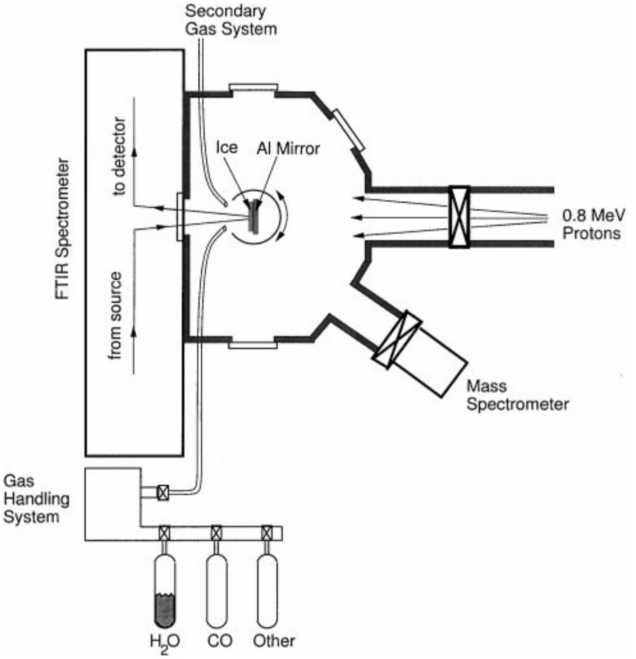


FIG. 1. Schematic of experimental set-up showing FTIR spectrometer, gas handling system, protons from Van de Graaff accelerator, and ice sample.

A closed-cycle cryostat was used to control the temperature of all samples from a minimum near 16 K up to about 280 K, with an accuracy better than ±1 K. Ice thicknesses were on the order of a few micrometers and were measured with a laser interference system assuming an index of refraction of 1.3 for our H_2O-dominated ices (Hudgins *et al*. 1993). Deposition rates were roughly 1–5 μm h^{-1}.

Abundances of radiation products were determined by integrating IR bands and dividing by the appropriate absolute band strengths, *A* values, measured by us (Hudson and Moore 1997, Moore and Hudson 1998) and others (e.g., Hudgins *et al*. 1993). This resulted in molecular abundances expressed as column densities with units of molecules cm^{-2}. Table II lists IR absorption bands used in this paper, along with the corresponding full-width at half maximum (FWHM) and *A* value for each band.

Although standard methods could be used in determining most *A* values, two cases demanded special consideration. A band observed near 1853 cm^{-1} in photolyzed $H_2O + CO$ and $H_2O + H_2CO$ ices has been attributed to the formyl free radical (HCO) by Allamandola *et al*. (1988). We observed a similar feature in our radiation experiments. To determine the integrated absorbance of this band, namely *A* (1853 cm^{-1}), we exposed an irradiated $H_2O + H_2CO$ ice, whose spectrum showed this feature, to unfiltered visible light from a 60-W tungsten lamp. The 1853-cm^{-1} absorbance was removed over a few hours and a concomitant increase in CO was found. These observations support the assignment of this band to HCO, the photobleaching being due to the reaction $HCO \rightarrow H + CO$. From the decrease in HCO at 1853 cm^{-1}, the increase in CO at 2137 cm^{-1}, and CO's known band strength, *A* (1853 cm^{-1}) for HCO was calculated to be 2.1×10^{-17} cm $molecule^{-1}$. Although the HCO band is rather broad and its maximum uncertain, it is certainly between 1850 and 1853 cm^{-1} (see IJzendoorn *et al*. (1983) for earlier work on HCO in ices other than $H_2O + CO$).

The other case requiring special consideration was HCOOH, formic acid. Because of the tendency of this molecule to complex with water, we made reference measurements on it using separate vacuum lines for simultaneously depositing H_2O and HCOOH. The pressure drop in each vacuum line gave the amount of each material in the final solid mixture, after correction for the fact that the gas-phase HCOOH (∼15 Torr, ∼295 K) used to make the solid was about 75% dimeric (Coolidge 1928). Our final *A* value for HCOOH monomers in H_2O ice is given

TABLE II
Spectral Values for Organic Molecules in Amorphous H_2O Ice at ∼16 K

Molecule	Average ratio H_2O : molecule	Vibrational mode	FWHM (cm^{-1})	Average band position (cm^{-1})	Integrated absorbance (*A*) (cm $molecule^{-1}$)
CO	20 : 1	C≡O st	9	2137	1.7×10^{-17}[c]
HCO[a]		C=O st	12	1853[b]	2.1×10^{-17}
H_2CO	20 : 0.6	H_2 scissor	11	1496	4.0×10^{-18}[d]
HCOOH	13 : 1	C–O st	60	1219	1.5×10^{-17}
CH_3OH	10 : 1	C–O st	∼22	1017	1.5×10^{-17}[e]
CH_4	15 : 1	C–H bend	12	1302	6.6×10^{-18}
CO_2	20 : 1	C=O st	7	2342	2.1×10^{-16}[f]

[a] Starting mixture was $H_2O + H_2CO$ (5 : 1).
[b] The corresponding position for $HC^{18}O$ was 1806 cm^{-1}.
[c] Standford *et al*. (1988).
[d] Schutte *et al*. (1993).
[e] Hudgins *et al*. (1993), weak interstellar mixture.
[f] Sandford and Allamandola (1990).

in Table II as 1.5×10^{-17} cm molecule^{-1}. Note that ISO spectra suggesting $H_2O + HCOOH$ ices associated with protostellar sources (Schutte *et al.* 1996b, 1998) have been analyzed using an *A* value based on that of gas-phase HCOOH dimers (Maréchal 1987).

Irradiations were done with a proton beam current of 0.1 μA and incident fluences of 1×10^{13} p$^+$ cm^{-2}–1×10^{15} p$^+$ cm^{-2}, although higher doses were used in a few experiments. Converting incident fluences into absorbed energy doses with units of eV molecule^{-1} required a value for each sample's stopping power, which in turn required each sample's density. Since the densities largely were unknown they were assumed to be 1 g cm^{-3}. For pure H_2O this gave an incident fluence of 8.8×10^{14} p$^+$ cm^{-2} as equivalent to an absorbed dose of 10 eV molecule^{-1}. For mixed ices, the stopping powers used were the weighted averages of stopping powers for each initial component. Additional details are given in Hudson and Moore (1995) and Moore and Hudson (1998). With ice sample thicknesses of 1–2 μm, the incident 0.8-MeV protons, having a range of 16 μm (Northcliffe and Shilling 1970), penetrated each sample and came to rest in the underlying aluminum substrate where the resulting current was integrated. In other words, little, if any, ion implantation took place.

The choice of 0.8-MeV protons to simulate cosmic ray bombardment requires comment. High-energy protons form the bulk of cosmic radiation particles, and of these the abundance of protons with energies in the 1-MeV region is much greater than for those with energies near 1 GeV (Meyer *et al.* 1974). Furthermore, standard tables show that the maximum stopping power for p$^+$ corresponds to an energy near 1 MeV (Northcliffe and Shilling 1970). The conclusion is that a substantial fraction of the cosmic ray damage to astronomical objects is expected to be due to protons with energies near 1 MeV. Further details can be found in earlier papers (Moore *et al.* 1983). We also note that recent work by Cooper *et al.* (1998) shows that protons form an important component of the energy flux received by Europa, Ganymede, and Callisto. Although our work was originally motivated by applications to comets and ISM ices, it also is relevant to icy satellites.

RESULTS

$H_2O + CO$ Experiments

Experiments were done with three different $H_2O:CO$ ratios, $H_2O:CO = 5$, 10, and 20. Figure 2 shows IR spectra for an ice analog made with $H_2O:CO = 5:1$. The spectrum of the unirradiated mixture is shown along with spectra after two proton irradiations, corresponding to radiation exposures of several meters down in a comet after about 2.3 and 4.6 billion years in the Oort Cloud (Strazzulla and Johnson 1991). In Fig. 2 absorptions of H_2O dominate the spectrum both before and after irradiation, but the production of CO_2 (2342 cm^{-1}) at the expense of CO (2137 cm^{-1}) is easily seen. (CO_2 was not studied extensively in these experiments. See Moore *et al.* (1991) for the CO_2/CO interconversion). Figure 3 is an enlargement of the region 1900–1000 cm^{-1} for the lower dose of Fig. 2. This spectral region shows that H_2CO (formaldehyde), HCOOH, CH_3OH (methanol), and CH_4 (methane) were synthesized from the initial $H_2O + CO$ mixture. Table III summarizes the abundances and radiation yields observed in these $H_2O + CO$ experiments. Figure 4 plots abundances for a number of molecules in the $H_2O:CO = 5$ experiment. Experiments on ices with lower initial CO abundances showed similar trends, with no additional new products being detected.

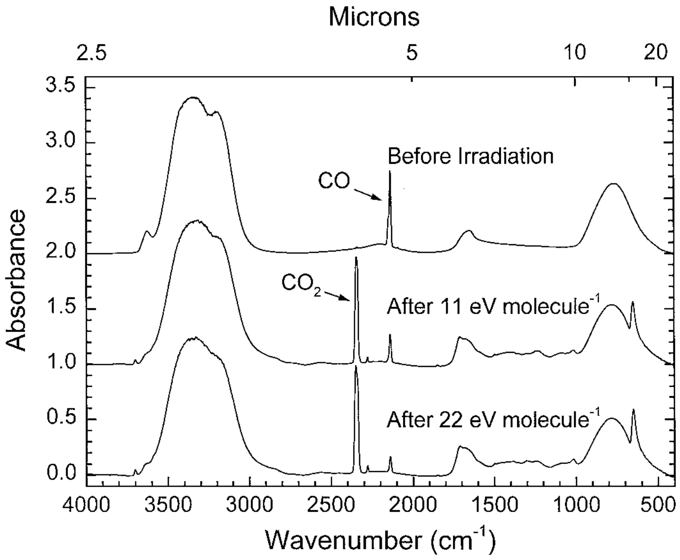


FIG. 2. Mid-infrared spectrum of an $H_2O + CO$ (5 : 1) ice 16 K before and after proton irradiation to two different doses. Spectra have been offset for clarity.

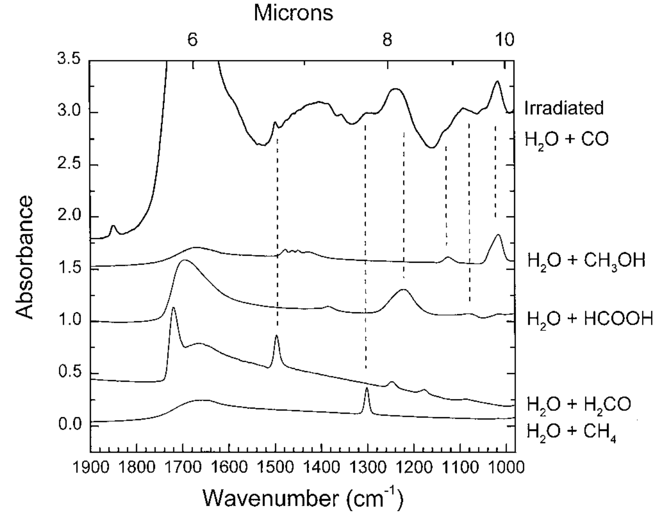


FIG. 3. New species formed in an $H_2O + CO$ (5 : 1) ice irradiated to 11 eV molecule^{-1} are identified by comparison with reference spectra of dilute mixtures of organics (H_2O : organic ≥ 5) at ~16 K. Spectra have been offset for clarity.

TABLE III
Comparison of Molecules Present after 22 eV Molecule^{-1} in H_2O + CO Ices with Different Initial Concentrations

New species identified	Mixture 5 : 1	Column density	G	Mixture 10 : 1	Column density	G	Mixture 20 : 1	Column density	G
	H_2O [5]			H_2O [10]			H_2O [20]		
	CO [1]	6.87×10^{17}		CO [1]	1.86×10^{17}		CO [1]	8.53×10^{16}	
	ΔCO	5.50×10^{17}	−0.7	ΔCO	1.67×10^{17}	−0.39	ΔCO	7.84×10^{16}	−0.2
HCO		4.88×10^{15}	0.006		1.28×10^{15}	0.003		1.10×10^{15}	0.003
H_2CO		3.71×10^{16}	0.05		1.48×10^{16}	0.03		9.01×10^{15}	0.02
HCOOH		2.22×10^{17}	0.28						
CH_3OH		6.34×10^{16}	0.08		1.23×10^{16}	0.03		2.33×10^{15}	0.006
CH_4		2.46×10^{17}	0.32		4.15×10^{16}	0.1		8.04×10^{15}	0.02
CO_2		1.28×10^{17}	0.16		6.59×10^{16}	0.16		3.60×10^{16}	0.09

Near 1850 cm^{-1} in both Figs. 2 and 3 is a feature commonly attributed to the formyl radical HCO. This band was easily removed with visible light, as explained under Experimental, an observation supporting its assignment to HCO. We measured the band strength at 1853 cm^{-1} as $A = 2.1 \times 10^{-17}$ cm molecule^{-1}. This is, to our knowledge, the first determination of this number in frozen H_2O.

In support of the above $H_2O + CO$ experiments, an ice with $H_2O : C^{18}O = 5 : 1$ was irradiated and the products were observed with IR spectroscopy. Isotopic shifts from the band positions of Table II were observed for the radiation products HCO, H_2CO, and CH_3OH, but little shift ($<$10 cm^{-1}) was seen for the broad band of HCOOH.

Last, a few complex ices were irradiated, and H_2CO, HCOOH, and CH_3OH were seen in each case. Specifically, we observed changes similar to those in binary mixtures after irradiation of $H_2O + CO + C_2H_2$ and $H_2O + CO + CH_4$ three-component mixtures and a $H_2O + CO + C_2H_2 + CH_4$ four-component mixture.

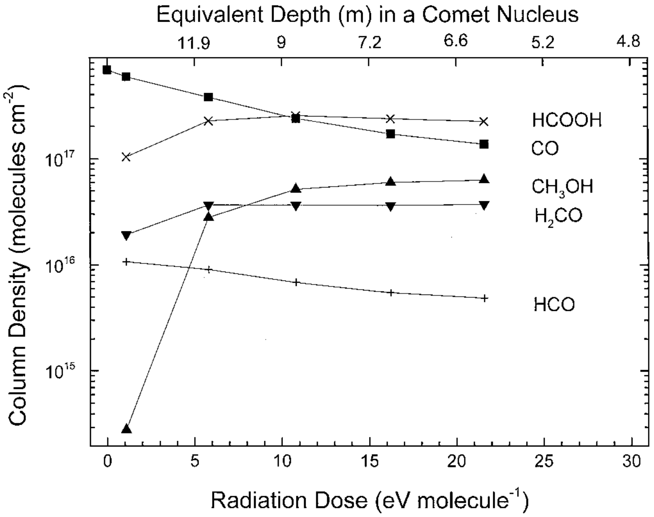


FIG. 4. Changes in the column density of molecules in an $H_2O + CO$ (5 : 1) ice as a function of radiation dose (lower x-axis) at ∼16 K. The upper x-axis shows the equivalent depth in a 0.3 g cm^{-3} comet nucleus at which a similar accumulated radiation dose is possible after 4.6 billion years of cosmic ray bombardment.

$H_2O + H_2CO$ Experiments

Figure 4 shows that during the irradiation of $H_2O + CO$, the abundance of HCO initially rose, but then fell with increasing dose. The same was true for H_2CO, although its decline was far slower than that for HCO and is more difficult to see in Fig. 4. On the other hand, in all experiments the CH_3OH abundance continuously increased. This behavior suggested that HCO and H_2CO were intermediates in the formation of CH_3OH from CO, the reaction sequence being

$$CO \rightarrow HCO \rightarrow H_2CO \rightarrow CH_3O \text{ and } CH_2OH \rightarrow CH_3OH.$$

Assuming this sequence to be correct, then H_2CO should be reduced to CH_3OH by ion irradiation of $H_2O + H_2CO$ mixtures. To test this idea, separate experiments with H_2CO were carried out. Ice samples having $H_2O : H_2CO = 5$ and 10 were irradiated and IR spectra recorded. Figure 5 shows spectra from one such experiment, and the conversion from H_2CO to CH_3OH is evident. Weaker features are also seen, and some assignments are indicated in the figure. Table IV gives product yields and molecular ratios at various stages of irradiation. Figure 6 shows how the H_2CO abundance decreased and the CH_3OH abundance increased with dose in the $H_2O : H_2CO = 5$ experiment.

In the reaction from H_2CO to CH_3OH, there is some uncertainty as to what free radical is formed by H-atom addition to H_2CO. In our experiments with $H_2O + H_2CO$ mixtures, enlargements of spectra in the region 1500–1000 cm^{-1} revealed several IR bands that rose and then fell with increasing radiation dose, peaking at ∼5 eV molecule^{-1}. Specifically, absorbances at 1456 and 1050 are almost certainly due to CH_2OH radicals (Jacox 1981), while a feature at 1033 cm^{-1} may be due to CH_3O radicals (Ohbayashi *et al.* 1977; Engelking *et al.* 1978; Inoue *et al.* 1980). Lacking integrated absorbances (A values), nothing quantitative can be said about the abundance of either radical.

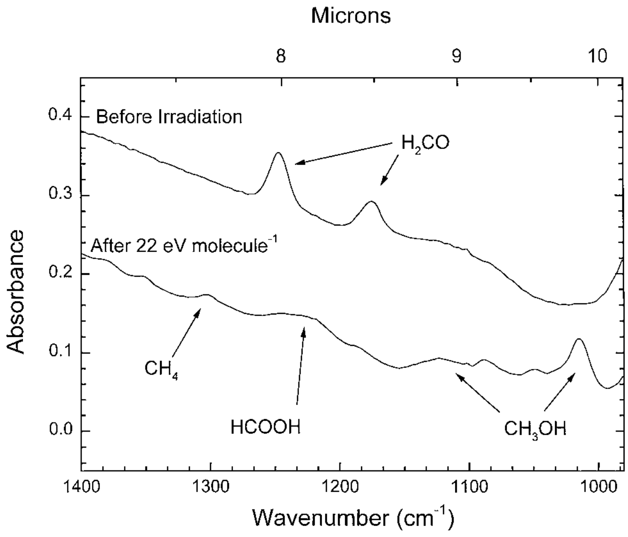


FIG. 5. Spectrum of an $H_2O + H_2CO$ (5 : 1) ice (1400–980 cm^{-1}) at ∼16 K before and after irradiation. Spectra have been offset for clarity and new species are labeled.

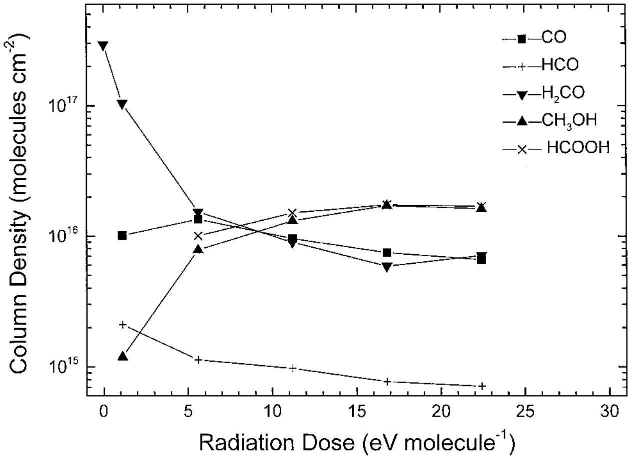


FIG. 6. Changes in the column density of molecules in an $H_2O + H_2CO$ (5 : 1) ice as a function of radiation dose at ∼16 K.

$H_2O + HCOOH$ Experiment

Experiments on $H_2O + CO$ and $H_2O + H_2CO$ mixtures gave HCOOH as a product of irradiation. To look at the fate of HCOOH, a separate radiation experiment was performed with an ice mixture initially having $H_2O : HCOOH = 20$ (spectra not shown). Loss of HCOOH and production of H_2CO and CH_3OH were observed, along with the synthesis of HCO, CO_2, and CH_4.

DISCUSSION

Insight into the radiation chemistry of cometary and interstellar ices requires an understanding of irradiated solid H_2O. Investigations since the early years of this century have left little doubt about the principal reactions occurring in frozen water (Spinks and Woods 1990; Hudson and Moore 1992 and references therein). Ionizing radiation, such as the incident protons in our radiation beam, initiates a series of ionizations and excitations in frozen H_2O molecules, with ionization being the dominant event. Rapid H^+ transfer, followed by neutralization of H_3O^+, produces H atoms and OH radicals. These reactions can be summarized as

$$\begin{aligned} H_2O &\rightarrow H_2O^+ + e^- \text{ (by radiation)} \\ H_2O^+ + H_2O &\rightarrow H_3O^+ + OH \\ H_3O^+ + e^- &\rightarrow H_2O + H. \end{aligned}$$

The net result is that H and OH are produced as reactive species. Subsequent combination of H and OH will regenerate H_2O, H atoms can combine to form H_2, and OH radicals can combine to make H_2O_2:

$$\begin{aligned} H + OH &\rightarrow H_2O \\ H + H &\rightarrow H_2 \\ OH + OH &\rightarrow H_2O_2. \end{aligned}$$

TABLE IV
Comparison of Molecules Present after 22 eV Molecule^{-1} in $H_2O + H_2CO$ Ices with Different Initial Concentrations

New species identified	Mixture 5 : 1	Column density	*G*	Mixture 10 : 1	Column density	*G*
	H_2O [5]			H_2O [10]		
	H_2CO [1]	3.00×10^{17}		H_2CO [1]	6.10×10^{16}	
	ΔH_2CO	2.93×10^{17}	−0.86	ΔH_2CO	5.90×10^{16}	−0.42
CO		6.58×10^{15}	0.02		1.44×10^{15}	0.01
HCO		7.13×10^{14}	0.002		—	—
HCOOH		1.69×10^{16}	0.05		—	—
CH_3OH		1.62×10^{16}	0.05		1.78×10^{15}	0.01
CH_4		3.96×10^{15}	0.01		—	—
CO_2		2.53×10^{16}	0.07		1.31×10^{16}	0.09

The products we observe in our spectra indicated that H and OH participated in additional reactions. Specifically, H atoms combined with CO generating H_2CO and then CH_3OH:

$$H + CO \rightarrow HCO$$
$$H + HCO \rightarrow H_2CO$$
$$H + H_2CO \rightarrow CH_3O \text{ and/or } CH_2OH$$
$$H + CH_3O \text{ and/or } CH_2OH \rightarrow CH_3OH.$$

Our $H_2O + C^{18}O$ radiation experiment supports this path to H_2CO and CH_3OH. The ^{18}O appeared in the carbonyl groups of $HC^{18}O$ and $H_2C^{18}O$, and, ultimately, the C–O bond of $CH_3^{18}OH$. These observations showed that the original pair of atoms in $C^{18}O$ remained bonded while the molecule was reduced by H atoms.

Besides the above reactions, our detection of HCOOH implies that H and OH combined with CO. Since no HO–C=O ($\sim$1800 cm^{-1}) radicals were detected, the sequence appears to be

$$H + CO \rightarrow HCO$$
$$OH + HCO \rightarrow HCOOH.$$

Again, our $H_2O + C^{18}O$ radiation experiment supports these reactions. HCOOH has both a C=O double bond and a C–O single bond. If the above two-step sequence is correct then irradiating $H_2O + C^{18}O$ should result in $HC^{18}O^{16}OH$ with a C=^{18}O double bond and a C–^{16}O single bond. One then expects, to a first approximation, only a small isotopic shift for the single bond, the C–O stretch, which we monitored (Table I). Our IR spectra confirmed this and so support the above sequence for HCOOH synthesis. For the sake of completion we add that a C=O isotopic shift of $\sim$30 cm^{-1} around 1700 cm^{-1} was seen in the $H_2O + C^{18}O$ radiation experiment and that it was most likely due to isotopic shifts from both $H_2C^{18}O$ and $HC^{18}OOH$.

Further H-atom addition to HCOOH will produce an unstable molecule, $H_2C(OH)_2$, which will decompose to H_2CO and in turn go on to form CH_3OH:

$$2H + HCOOH \rightarrow H_2C(OH)_2 \rightarrow H_2CO + H_2O$$
$$2H + H_2CO \rightarrow CH_3OH.$$

Although destruction of HCOOH is supported by our $H_2O +$ HCOOH experiment, Fig. 4 shows that this process is not significant in the more relevant $H_2O + CO$ ices. There the HCOOH abundance rises with dose, but with little or no subsequent decline.

Our spectra also contained weak bands which rose and fell in intensity as the irradiations took place. A weak IR absorbance near 1853 cm^{-1} has long been associated with HCO (Allamandola *et al*. 1988), and our photobleaching experiment, in which this band was removed and CO production observed, supports this assignment, as does the ^{18}O substitution experiment. That this HCO feature grew and then fell in intensity early in the $H_2O + CO$ irradiation is consistent with a role as an intermediate en route to H_2CO. Similarly, spectral features assigned to CH_2OH and CH_3O radicals in the $H_2O + H_2CO$ experiments showed a rise and fall in intensity with radiation dose, again the behavior expected for intermediates on the path from H_2CO to CH_3OH.

It should be noted that the H-atom reactions observed were not limited to two-component ice mixtures, but that they also took place in more complex ones as well. For example, the presence of C_2H_2, to which H atoms readily add (Moore and Hudson 1998), did not prevent the conversion of CO into H_2CO, HCOOH, and CH_3OH. CO and C_2H_2 reacted as if each was independent of the other, with the chemistry being dominated by H and OH addition reactions.

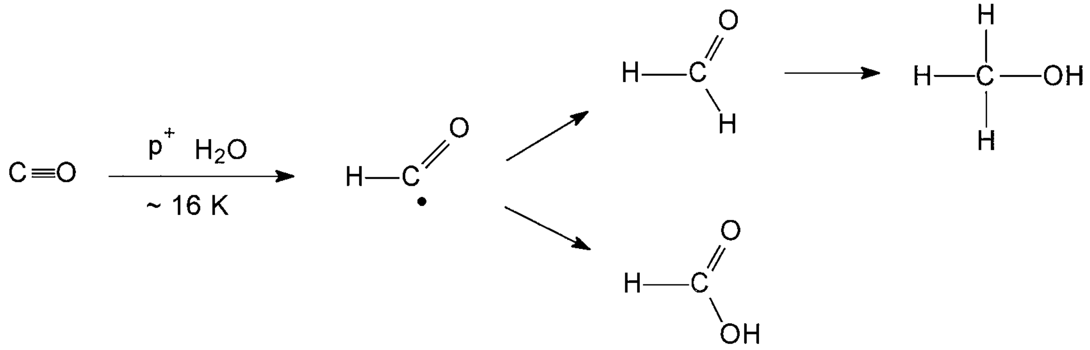
There are several ways to quantitatively examine the products of our reactions. Radiation yields are often expressed as *G* values, the number of molecules altered per 100 eV of energy absorbed. These are listed for our $H_2O + CO$ and $H_2O + H_2CO$ experiments in Tables III and IV, respectively. For the dose in Table III, $G(H_2CO)$ and $G(CH_3OH)$ increases with initial concentration of CO. Similarly, for a given dose, $G(CH_3OH)$ increases with initial concentration of H_2CO. This dependence of *G* values on initial concentrations was noted earlier (Moore and Hudson 1998). Finally, the *G* values in radiation chemical studies are often calculated for small doses and reflect the kinetics of product formation. However, the products of our reactions were close to their equilibrium abundances at the doses used to calculate *G*'s. For this reason, sufficient information is provided in the figures and tables to rescale our *G*'s to smaller doses.

Scheme 1 shows the CO reaction pathways followed in our work. The lower branch, leading from HCO to HCOOH, constitutes a "dead end" as little HCOOH is converted into other products. However, the upper branch leads from H_2CO to CH_3OH. Table III shows that the combined column densities of H_2CO and CH_3OH in our 5 : 1 experiment are only about half that of HCOOH. This implies that the branching ratio from HCO in the above diagram is about 2 : 1 in favor of HCOOH. Coincidentally, the other two stable products listed in Table III have $CH_4 : CO_2 \approx 2 : 1$, assuming that the entire 1300-cm^{-1} feature is due to methane. Combining all these numbers gives

$$(H_2CO + CH_3OH) : HCOOH : CH_4 : CO_2 \approx 1 : 2 : 2 : 1$$

for our $H_2O : CO = 5 : 1$ experiment. This demonstrates that although CH_4 and CO_2 were not the focus of our experiments, they clearly play an important role in the radiation chemistry of $H_2O + CO$ ices. CH_4 and CO_2 will be treated in a separate paper.

One of our most important findings is the relatively high percentage of conversion of CO into other molecules. For the highest radiation dose of Fig. 2, about 22 eV molecule^{-1}, the conversion of CO to HCOOH was surprisingly large, almost 40%, and the CO to H_2CO conversion was 7%. The overall yield from CO



SCHEME 1

to CH_3OH for this same radiation dose was about 12%. Adding the 7% H_2CO yield to this 12%, since CH_3OH forms from CO by way of H_2CO, gives the total conversion CO → H_2CO as 19%. This can be compared with the ~5% conversion reported for UV-photolysis experiments on $H_2O + CO$ mixtures (Schutte *et al.* 1996a) or the ~0.015% conversion observed in discharge experiments (Hiraoka *et al.* 1998). In those same discharge experiments, H_2CO and CH_3OH molecules were detected only on warming ice mixtures to ~100 K, although molecular formation was inferred from the experimental conditions. Our IR experiments clearly show H_2CO and CH_3OH formation at the lowest ice temperatures ($T \sim 16$ K).

In evaluating the products in our experiments, the distinction between molecules formed and molecules observed must be kept in mind. In H_2O-dominated ices, weak spectral features near intense H_2O absorptions are difficult to detect. The spectral "windows" that proved the clearest and most valuable for product identification were roughly 3000–1700 and 1600–1000 cm^{-1}. Fortunately, the expected products in our experiments, and most other molecules of interest, had IR absorptions in one or both of these regions.

As our experiments progressed, an important chemical pattern emerged. We found that in $H_2O + CO$ ices, *only* single-carbon products, namely H_2CO, HCOOH, and CH_3OH, were observed. (CO_2 and CH_4 were also formed, although they were not studied extensively in these experiments.) Searches were made in our spectra for evidence of two-carbon molecules (e.g., C_2H_2, C_2H_4, C_2H_5OH, C_2H_6, CH_3CHO, C_2O_3, CH_3COOH) and three-carbon molecules (e.g., C_3H_8, C_3H_6, CH_2CCH_2, $HCCCH_3$, $CH_3CH(OH)CH_3$, $CH_3CH_2CH_2OH$, $CH_3C(O)CH_3$). No such molecules were expected, and indeed all such searches were unsuccessful. Neither was polymeric material, for example, a formaldehyde polymer, nor any polycyclic aromatic hydrocarbon (PAH) molecule ever found. In all experiments, single-carbon molecules dominated the radiation products of both $H_2O + CO$ and $H_2O + H_2CO$ ices. This behavior stands in marked contrast to radiation studies of pure hydrocarbons (Kaiser and Roessler 1992) or pure CO (Palumbo and Strazzulla 1993), or the UV-photolysis of pure materials (Gerakines *et al.* 1996). In experiments on pure (one-component) ices, lengthening of a carbon chain appears quite common, while in our highly polar, H_2O-dominated ices it was never observed.

Astrochemical Implications

Interstellar grains, from which comets and other Solar System objects are thought to form, serve as reaction sites for molecules. Molecular formation can occur both on grain surfaces (Tielens and Hagen 1982) and, through energetic processing, beneath grain surfaces (Moore *et al.* 1983; Strazzulla and Johnson 1991; Shalabiea and Greenberg 1994). Our experiments are most closely related to radiation processing of interstellar grain mantles and also to the surfaces of solar system objects. As H_2O-dominated ices are processed by cosmic radiation we expect that CO will react with H atoms and OH radicals to form HCOOH, H_2CO, and CH_3OH. Other molecules present in a "dirty" ice may influence the final product distribution, but as long as H_2O dominates the ice we expect H and OH additions to CO and other unsaturated molecules.

In an earlier paper we showed that CH_3OH is made in irradiated $H_2O + CH_4$ mixtures (Moore and Hudson 1998). It is appropriate to compare those results with the present work. Table III can be used to calculate CH_3OH percentage yields from ices initially with $H_2O : CO = 20$, 10, and 5 as 3, 7, and 12%, respectively. Thus, the CO → CH_3OH conversion rises with CO's initial abundance. In contrast, the data from Table III of our earlier paper give $CH_4 \rightarrow CH_3OH$ yields as roughly constant at ~15% for $H_2O : CH_4$ initial ratios of 15, 7, and 2. Although this seems to imply that more CH_3OH can be made from CH_4 than CO in cometary and interstellar ices, the much higher abundance of CO (Table I) will allow it to dominate CH_3OH production.

In addition to relatively stable molecules, such as H_2CO, HCOOH, and CH_3OH, our experiments have identified free radicals in proton-irradiated cometary and interstellar ice analogs. HCO was seen in experiments beginning with either $H_2O + CO$ or $H_2O + H_2CO$. Previously we showed that in H_2O irradiated at ~13 K, the concentration of H and OH radicals rises until it becomes high enough to initiate a chemical chain reaction (Hudson and Moore 1992). At that point the ice temperature can rise by over 100 K, causing ice crystallization and, in a small-scale explosion, loss of sample material. In the case of cometary, planetary, or interstellar ices, some H atoms will be "scavenged" by CO and form HCO radicals, but rapid heating may still initiate a free-radical chain reaction as seen in pure H_2O. This scenario apparently was first proposed by Donn and Urey (1956) to explain cometary outbursts, but has since been studied by others (Leger *et al*. 1985).

Although H_2CO and CH_3OH have been studied in ices for some time (Allamandola *et al*. 1988; Schutte *et al*. 1996a), much less work has been done with HCOOH. Our experiments suggest that energetic processing can readily produce HCOOH in H_2O-dominated ices, although the detection of this molecule in the solid state will be challenging. The intense carbonyl (C=O) stretch of HCOOH near 1700 cm^{-1} (5.88 μm) will not be a good indicator of HCOOH's presence as H_2CO, and many aldehydes, ketones, and carboxylic acids, have features in the same region. A slightly weaker absorption near 1220 cm^{-1} (8.20 μm) might be a much better indicator of HCOOH, but it borders on the intense interstellar silicate band. Another complication is that HCOOH, being an acid, will react with NH_3, a known grain molecule, reducing the intensity of all HCOOH features.

The CO reactions we have studied will contribute to the CH_3OH abundance in interstellar ices before they accrete to form macroscopic objects. Also, before a comet passes about the Sun it will be subjected to cosmic radiation while in the Oort Cloud. This will convert additional CO into CH_3OH, the greatest conversion being at a comet's surface. The top scale of Fig. 4 gives the depth calculated in a comet nucleus at which the ices receive a radiation dose (accumulated over 4.6 billion years) corresponding to the bottom scale. With the upper scale the curves shown provide a rough idea of how molecular abundances will vary with depth in a comet dominated by frozen H_2O and CO. It can be seen that as one passes from deep in a comet toward its surface that the ratio $(CH_3OH)/(H_2CO)$ grows, eventually reaching $\sim$1.7 after 22 eV molecule^{-1}. For comparison, this ratio is $\sim$2 for the comets and the interstellar ice in Table I.

Aside from radiation dose, $(CH_3OH)/(H_2CO)$ also was found to vary directly with initial CO concentration, as can be seen from the data in Table III. This is understandable from the reaction mechanism proposed and even lends support to it. With a "large" initial amount of CO in a cometary or interstellar ice one expects greater conversion to CH_3OH and smaller remaining H_2CO.

Although this paper has focused on the production of CH_3OH, this molecule's abundance in astronomical ices also depends on how fast it, in turn, might be converted into other materials. In reading the literature one sometimes encounters statements about the apparent sensitivity of CH_3OH and its ease of destruction (e.g., Schutte *et al*. 1993; Teixeria *et al*. 1998). However, essentially all small organic molecules will be sensitive to destruction by cosmic radiation and UV photons. Published statements about the "sensitivity" of CH_3OH apparently arise from laboratory work on the irradiation (Moore *et al*. 1996) or UV-photolysis (Gerakines *et al*. 1996) of pure CH_3OH, or the irradiation (Strazzulla *et al*. 1995) or UV-photolysis (Allamandola *et al*. 1988) of mixtures with high initial CH_3OH abundances. Under such conditions, a relatively high reaction *rate* for CH_3OH destruction will be measured, and such will be the case for almost any organic molecule. For the specific case of CH_3OH, irradiation yields both CH_3O and CH_2OH radicals (Wargon and Williams 1972). These will undergo disproportionation reactions, such as

$$CH_3O + CH_3O \rightarrow H_2CO + CH_3OH,$$

to form H_2CO (Spinks and Woods 1990). However, the importance of such radical–radical reactions falls with initial CH_3OH concentration. In other words, laboratory experiments using "high" abundances of CH_3OH will show a high rate of CH_3OH destruction and H_2CO formation, but if CH_3OH forms in a H_2O-dominated ice, such as in the work presented in this paper, it will appear stable against further change. This suggests that in an astronomical environment, such as an interstellar grain exposed to cosmic rays, CH_3OH will grow as long as there is CO and H_2CO to be processed. When those two precursors are depleted, or when the grain has been processed to where H_2O no longer dominants the grain mantle, then the abundance of CH_3OH will decline as shown in laboratory studies (Allamandola *et al*. 1988; Strazzulla *et al*. 1995; Moore *et al*. 1996; Gerakines *et al*. 1996).

This leads to an important consideration in applying laboratory ice experiments to interstellar and solar system problems: the ice composition *cannot* be neglected. Chemical reactions that occur in pure ("neat") materials may play only minor roles in mixed molecular ices. A laboratory observation of a reaction in, for example, pure CO cannot be used to argue that the same reaction occurs in interstellar or cometary grains in which solid H_2O may control the chemistry. Along these lines, our work applies most directly to the polar ices thought to dominate comets and many satellite surfaces. In contrast, the radiation chemistry of nonpolar ices remains largely unexplored.

CONCLUSIONS

Our experiments have shown that solid-phase radiolysis of $H_2O + CO$ mixtures generates organic molecules, such as H_2CO, HCOOH, and CH_3OH, with greater abundances than reported to date. Product yields have been measured and tabulated for applications such as ion bombardment of Solar System and interstellar ices. Comparisons to earlier experiments have been made and demonstrate the importance of ice compostion in applying laboratory results to astrochemical problems. Absolute IR band strengths of HCO and HCOOH trapped in H_2O ice are reported for the first time. Finally, isotopic labelling has been used to support an H-atom addition mechanism for the low-temperature, solid-phase reaction sequence $CO \rightarrow H_2CO \rightarrow CH_3OH$.

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