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Energetic processing of laboratory ice analogs: UV photolysis versus ion bombardment

P. A. Gerakines[1] and M. H. Moore

Astrochemistry Branch, NASA Goddard Space Flight Center, Greenbelt, Maryland, USA

R. L. Hudson

Department of Chemistry, Eckerd College, St. Petersburg, Florida, USA

Abstract. We have the ability to perform both ultraviolet (UV) photolysis (primarily Lyman-α photons, average $E \approx 10.2$ eV per photon) and ion irradiation (protons, $E = 0.8$ MeV) in the same experimental setup, with ices created under identical conditions. Here we present recent results on the UV and ion processing of ice mixtures at 18 K of the composition $H_2O + CO_2 + CH_3OH$ (1:1:1) and $H_2O + CO_2 + CH_4$ (1:1:1). H_2O, CH_3OH, CH_4, and CO_2 are all major components of ices in most astrophysical environments (whether interstellar, cometary, or planetary). Identifications and formation rates of products were measured. Results for photolyzed and irradiated ices are contrasted. We find that similar chemical products are observed in both cases and that rates of formation are equivalent for most of the major products.

1. Introduction

Water (H_2O), carbon dioxide (CO_2), methane (CH_4), and methanol (CH_3OH) have all been identified as important constituents of various astrophysical environments. See *Gibb et al.* [2000] for a recent comparison of interstellar and cometary ices and Table 1 from *Hudson and Moore* [this issue] for a recent inventory of planetary ices. In most cases, especially in the interstellar medium and in comets, H_2O is the major ice component in which the others are diluted. All of these astrophysical environments are subjected to some form of energetic processing, whether it be from particles and ions (as part of, e.g., cosmic rays, the solar wind, or the magnetosphere of a gas giant planet) or from photons (e.g., the interstellar radiation field or solar ultraviolet light or x rays). However, the effects of these two very important processes are rarely compared in the literature. See Figure 1, adapted from *Spinks and Woods* [1990], for an illustration of the effects of photolysis and irradiation on an ice. We have recently published a comparison of carbonic acid (H_2CO_3) and CO production in UV-photolyzed and proton-irradiated $H_2O + CO_2$ ices at 18 K [*Gerakines et al.*, 2000]. Here we extend that work in a direct comparison of photolysis and irradiation of $H_2O + CO_2 + CH_3OH$ (1:1:1) and $H_2O + CO_2 + CH_4$ (1:1:1) ices at 18 K in the same laboratory, with ices created under the same conditions.

[1]Now at Astro- and Solar-System Physics Program, Department of Physics, University of Alabama at Birmingham, Birmingham, Alabama, USA.

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2. Experimental Procedure

The details of our experimental setup and procedures are given by, e.g., *Hudson and Moore* [1995], *Moore and Hudson* [1998], and *Hudson and Moore* [this issue]. In summary, gases are prepared inside a vacuum manifold and vapor-condensed onto a cold (18 K) aluminum mirror suspended inside a stainless-steel high-vacuum chamber ($P \approx 10^{-7}$ torr; see Figure 1 from *Hudson and Moore* [this issue] for a diagram of the setup). Mixing ratios in the resultant ice are determined from the partial pressures inside the manifold before condensation. IR spectra (with a spectral range of 4000-400 cm^{-1} and a resolution of 4 cm^{-1}) are taken by diverting the beam of a Fourier-transform infrared (FTIR) spectrometer (Mattson) toward the ice-covered mirror, where it passes through the ice before and after reflection at the ice-mirror interface. Reagents used and their purities are as follows: H_2O (triply distilled, with a resistance $>10^7$ ohm cm), CO_2 (gas, Matheson, 99.995%), CH_3OH (triply distilled, Aldrich, 99.9+%), and CH_4 (gas, Matheson, 99.999%).

Ices are processed by turning the mirror to face either a beam of 0.8 MeV protons generated by a Van de Graaff accelerator or a microwave-discharge hydrogen flow lamp that produces primarily Lyman-α photons ($E = 10.2$ eV). The UV lamp's flux at the ice sample was measured to be approximately 8.6×10^{13} photons cm^{-2} s^{-1}. The UV lamp system and this flux measurement are described in detail by *Gerakines et al.* [2000].

3. Results and Discussion

3.1. Products of the Energetic Processing

Figures 2 and 3 contain the full mid-IR (4000-500 cm^{-1}) ice spectra before and after processing, and Table 1 lists the observed products. In the case of the CH_3OH-containing ice

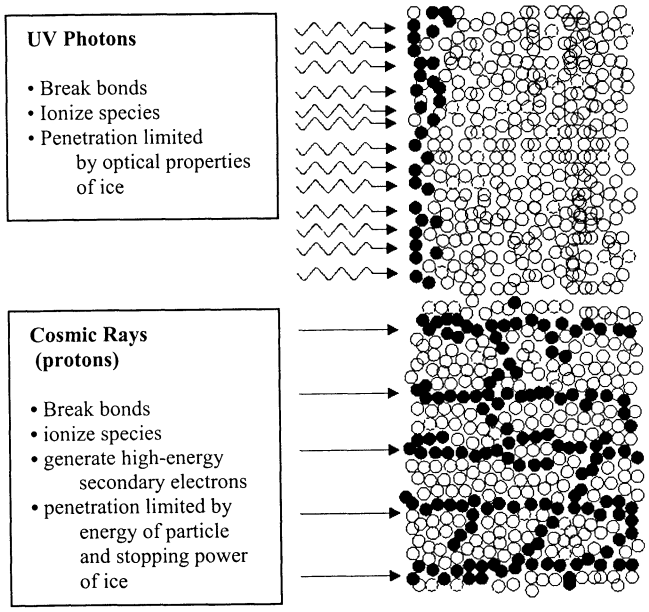

Figure 1. Illustration of ice-processing effects caused by UV and cosmic rays (adapted from *Spinks and Woods* [1990]).

(spectra displayed in Figure 2), the main products of both irradiation and photolysis were CO, H_2CO, ethylene glycol ($C_2H_4(OH)_2$), and HCO. Processing of the CH_4-containing ice (spectra displayed in Figure 3) produced all of these molecules, with the addition of ethane (C_2H_6), propane (C_3H_8), and possibly higher-order hydrocarbons.

Work already present in the literature [e.g., *Gerakines et al.*, 1996; *Moore and Hudson,* 1998] has shed light on how the individual components of out experiments behave under energetic processing. For instance, methanol produces CO, CO_2, CH_4, HCO, H_2CO, and $C_2H_4(OH)_2$ upon processing. The products of pure CH_4 processing are ethane, propane, and

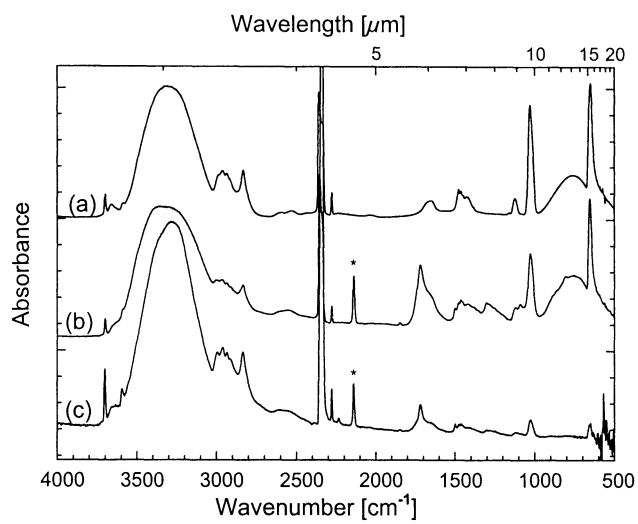

Figure 2. Mid-IR (4000-500 cm^{-1}) spectrum of an $H_2O + CO_2 + CH_3OH$ ice at 18 K (a) before processing, (b) after proton bombardment, and (c) after UV photolysis. Spectrum c has been scaled up by a factor of 12 so that the height of the CO band at 2139 cm^{-1} (indicated by asterisks) matches that of spectrum b.

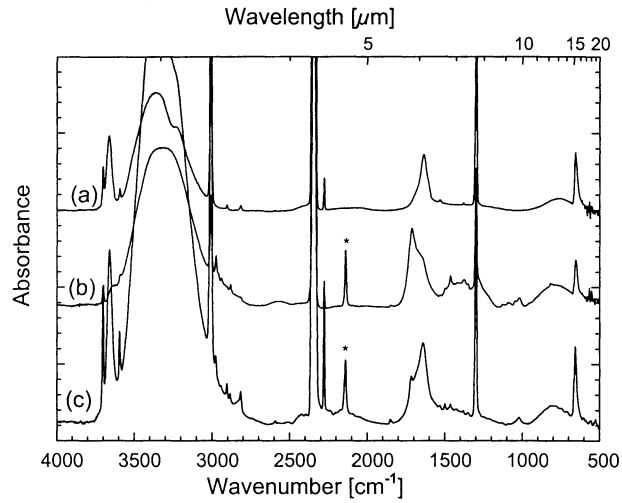

Figure 3. As Figure 2, but for an $H_2O + CO_2 + CH_4$ ice at 18 K. Spectrum c has been scaled up by a factor of 5 so that the height of the CO band at 2139 cm^{-1} (indicated by asterisks) matches that of spectrum b.

more complex aliphatic structures. When processed in mixtures with H_2O and CO_2, all of these species are produced. In the mixed ices, some few additional species are formed. For instance, methanol is produced from the $H_2O + CO_2 + CH_4$ ice, likely through the reaction of CH_3 (from CH_4) with OH (from H_2O).

The spectral region from 1420 to 1320 cm^{-1} is shown in Figures 4 and 5. Figure 4 shows a comparison of the proton-irradiated and UV-photolyzed $H_2O + CO_2 + CH_3OH$ ices, and Figure 5 shows the same comparison for the $H_2O + CO_2 + CH_4$ ice. While all the products described in the previous paragraph were found in both the photolysis and irradiation experiments, the formate ion, $HCOO^-$, whose absorption features fall near 1380 and 1350 cm^{-1}, is seen here only in the proton-irradiated ice (Figure 4). $HCOO^-$ has previously been identified as an irradiation product of both $H_2O + CH_3OH$ and

Table 1. Product Identifications

$H_2O + CO_2 + CH_3OH$		$H_2O + CO_2 + CH_4$	
Position cm^{-1}	Molecule	Position cm^{-1}	Molecule
2138	CO	2975	C_2H_6
1846	HCO	2960	C_3H_8 + larger
1718	H_2CO	2941	C_2H_6
1499	H_2CO	2904	C_3H_8 + larger
1380	$HCOO^-$	2883	C_2H_6
1353[a]	$HCOO^-$	2139	CO
1302	CH_4	1848	HCO
1250	H_2CO	1713	H_2CO
1089	$C_2H_4(OH)_2$	1498	H_2CO
861	$C_2H_4(OH)_2$	1464	C_2H_6
		1370	C_2H_6
		1352	CH_3HCO
		1128	CH_3OH
		1089	$C_2H_4(OH)_2$
		1046	$C_2H_4(OH)_2$
		1019	CH_3OH
		861	$C_2H_4(OH)_2$

[a]Observed only in the proton-irradiated ice.

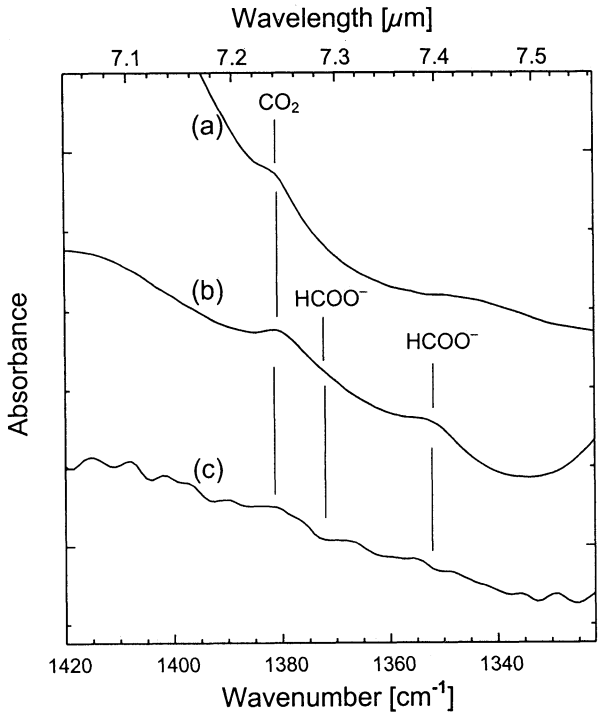

Figure 4. The 1420-1320 cm^{-1} spectral region from Figure 2 (with identical scaling factors).

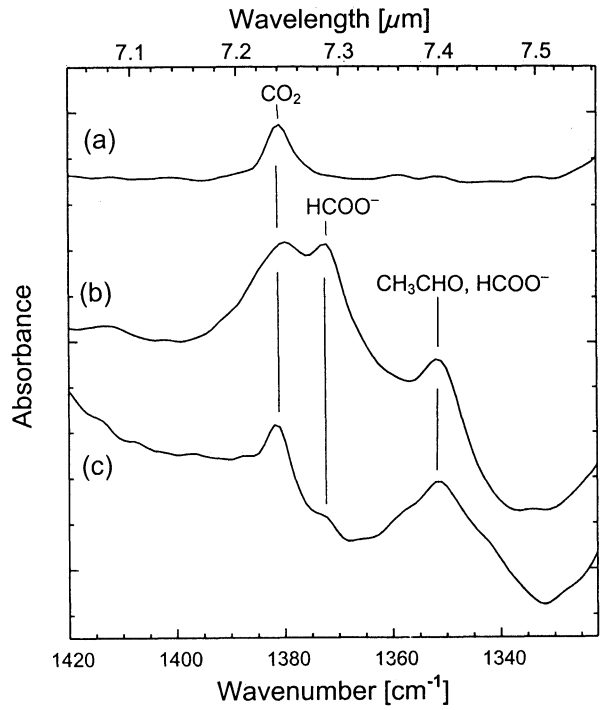

Figure 5. The 1420-1320 cm^{-1} spectral region from Figure 3 (with identical scaling factors).

H_2O + CO ices [*Hudson and Moore*, 2000; *Moore et al.*, 2001].

In contrast, a band appears at 1350 cm^{-1} in both the irradiated and photolyzed CH_4-containing ices (Figure 5). This band is consistent with the results of *Moore and Hudson* [1998], who tentatively proposed acetaldehyde (CH_3CHO) as the carrier species for this feature in irradiated H_2O + CH_4 ices. A band due to ethane (C_2H_6) is also present at 1372 cm^{-1} in each case (although weaker in the photolyzed ice). A band due to propane (C_3H_8) may contribute to the broad absorption near 1380 cm^{-1}.

3.2. Measurement of Production and Destruction Rates

To compare the production and destruction rates of species in the two types of experiments, the methods developed by *Gerakines et al.* [2000] have been used, involving only direct measurements from the experiments without a complex transformation from, e.g., cross sections for formation or destruction (as is typically reported for UV photolysis experiments [e.g., *Gerakines et al.*, 1996]). In summary, product yields were uniformly calculated from the processed ice spectra as is typical in irradiation experiments by measuring the column density of the product and the total energy absorbed by the ice sample (per unit area) at each stage of the exposure. Band strengths used to make the column density measurements were taken from *Gerakines et al.* [1995], *Moore and Hudson* [1998], *Hudson and Moore* [1999], and the references therein.

The absorbed energy is calculated by different means for irradiation and photolysis. In the case of the proton-irradiated ices the energy absorbed per unit area is the product of the integrated proton current, the stopping power of the ice, the ice density, and its thickness (see, e.g., *Moore and Hudson* [1998] for a detailed description of this calculation). For photolyzed ices the energy absorbed per unit area is merely the product of the UV lamp's photon flux (in cm^{-2} s^{-1}), the total exposure time (in s), and the average energy per photon (in eV). The ice must have sufficient thickness to ensure that as many incident photons are absorbed as possible. For an ice composed of pure H_2O, an ice thickness of 0.3 μm will absorb 90% of photons at 10.2 eV, on the basis of the UV absorption

Table 2. Yields per 100 eV of Formation and Destruction[a]

	$H_2O+CO_2+CH_3OH$		$H_2O+CO_2+CH_4$	
Species	*p*+	UV	*p*+	UV
CO_2	-0.2±0.2	-0.4±0.2	-0.6±0.2	-3±1
CH_3OH	-0.37±0.04	-0.5±0.2	0.10±0.05	0.14±0.03
CH_4	??	0.033±0.002	-0.6±0.2	-0.6±0.1
CO	0.19±0.03	0.71±0.08	0.27±0.07	0.55±0.02
H_2CO	0.3±0.3	0.4±0.2	0.04±0.01	0.16±0.07
HCO	0.008±0.005	0.017±0.001	0.010±0.008	0.026±0.005
C_2H_6	...	...	0.8±0.4	1.0±0.3

[a]Positive values indicate formation; negative values indicate destruction.

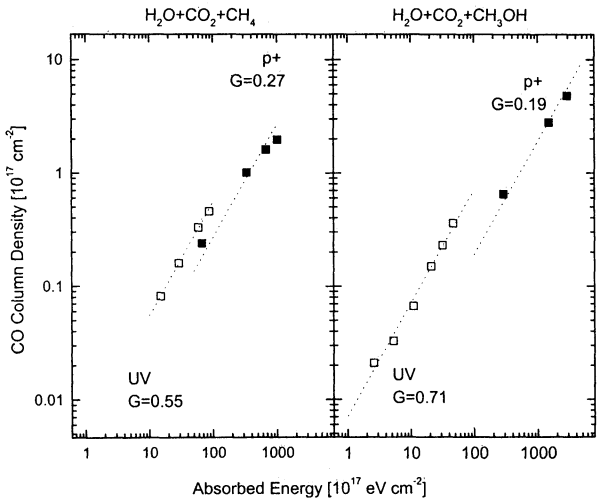

Figure 6. CO column density (in 10^{17} cm^{-2}) versus absorbed energy (in 10^{17} eV cm^{-2}) for the experiments involving (left) $H_2O + CO_2 + CH_4$ and (right) $H_2O + CO_2 + CH_3OH$. Solid symbols represent the irradiation experiments, and open symbols represent the photolysis experiments. Dotted lines represent the best fitting production rates in each case.

cross section for H_2O as given by *Okabe* [1978]. The yield in an experiment involving either irradiation or photolysis, expressed as the number of product molecules per 100 eV absorbed, is then calculated from the ratio of product column density *(N)* to the energy absorbed per unit area *(E)* as follows:

$$G = 100 \times N / E . \quad (1)$$

Values of *G* calculated from our experimental data in this way are presented in Table 2. Figure 6 displays the results for the production of CO in both sets of experiments.

Comparisons of calculated rates of formation in Table 2 show few differences between the products of irradiation and photolysis (given the listed 1-σ error bars). The greatest contrast is found for CO, which is formed 2-4 times more effectively by UV photolysis than by proton irradiation. There are also differences, although less dramatic, in the formation of H_2CO and HCO.

4. Summary

While it is generally accepted that the ices in astrophysical environments undergo processing, the dominant form of processing is not always clear. It is also generally assumed that ion bombardment and UV photolysis have similar effects on icy materials, but as illustrated in Figure 1, these processing methods are clearly not identical. One important difference between photolysis and irradiation is the penetration depth. In relation to our results, we have measured the formation rates in that part of the ice that is significantly processed. For the irradiated ices the entire bulk of the ice has been processed, but only the top few tenths of a μm are processed in the photolysis studies. In order to increase the level of processing by photolysis, the exposure would need to take place simultaneously with the condensation of the ice layer [see, e.g., *Gerakines et al.*, 2000). For planetary ices, therefore, particle bombardment should play a much greater role in processing bulk ices, such as the surface of Europa or the nuclei of comets. In the interstellar medium, where icy grain mantles are expected to be very thin, perhaps 0.01 μm, irradiation and photolysis should each contribute to the overall ice processing.

The presence of impurities in our ices may play a role in the interaction between the applied energy and the reactant ice species. We have not addressed this issue, since the main goal of this work is to contrast the differences between the bulk effects of photolysis and irradiation, but future work will study the effects of ice structure on product yields.

A diagnostic of a specific form of ice processing could provide the answer as to which form of processing dominates in the different regions under consideration. In this paper we have presented the results of both proton irradiation and UV photolysis experiments for ices of the composition $H_2O + CO_2 + CH_3OH$ (1:1:1) and $H_2O + CO_2 + CH_4$ (1:1:1). We have compared the major products and their rates of formation and found that while generally similar, at least two major differences exist: (1) the formate ion is observed only for proton-irradiated CH_3OH-containing ices, and (2) the rate of CO formation is measured to be 2-4 times higher in UV-photolyzed ices. The former difference is likely due to the fact that the secondary electrons produced by photolysis do not have enough energy to form stable negative ions, while those produced by proton bombardment are extremely energetic. The latter difference observed in our experiments is due to the fact that the dissociation energy of CO is 11.1 eV and beyond the range of the UV produced by the lamp used for laboratory photolysis experiments. Therefore the CO produced in the irradiation experiments is more easily broken down that in the photolysis experiments.

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References

Gerakines, P. A., W. A. Schutte, J. M. Greenberg, and E. F. van Dishoeck, The infrared band strengths of H_2O, CO, and CO_2 in laboratory simulations of astrophysical ice mixtures, *Astron. Astrophys., 296*, 810-818, 1995.

Gerakines, P. A., W. A. Schutte, and P. Ehrenfreund, Ultraviolet processing of interstellar ice analogs, I, Pure ices, *Astron. Astrophys., 312*, 289-305, 1996.

Gerakines, P. A., M. H. Moore, and R. L. Hudson, Carbonic acid production in H_2O+CO_2 ices – UV photolysis vs. proton bombardment, *Astron. Astrophys., 357*, 793-800, 2000.

Gibb, E. L., D. C. B. Whittet, W. A. Schutte, A. C. A. Boogert, J. E. Chiar, P. A. Gerakines, J. V. Keane, A. G. G. M. Tielens, E. F. van Dishoeck, and O. Kerkhof, An inventory of interstellar ices toward the embedded protostar W33A, *Astrophys. J., 536*, 347-356, 2000.

Hudson, R. L., and M. H. Moore, Far-IR spectral changes accompanying proton irradiation of solids of astrochemical interest, *Radiat. Phys. Chem., 45*, 779-789, 1995.

Hudson, R. L., and M. H. Moore, Laboratory studies of the formation of methanol and other organic molecules by water + carbon monoxide radiolysis: Relevance to comets, icy satellites, and interstellar ices, *Icarus, 140*, 451-461, 1999.

Hudson, R. L., and M. H. Moore, IR spectra of irradiated cometary ice analogues containing methanol: A new assignment, a reassignment, and a non-assignment, *Icarus, 145*, 661-663, 2000.

Hudson, R. L., and M. H. Moore, Radiation chemical alterations in solar system ices, *J. Geophys. Res.*, this issue.

Moore, M. H., and R. L. Hudson, Infrared study of ion-irradiated water-ice mixtures with hydrocarbons relevant to comets, *Icarus, 135*, 518-527, 1998.

Moore, M. H., R. L. Hudson, and P. A. Gerakines, Mid- and far-infrared spectroscopic studies of the influence of temperature,

ultraviolet photolysis and ion irradiation on cosmic-type ices, *Spectrochim. Acta*, *54*, 843-858, 2001.
Okabe, H., *Photochemistry of Small Molecules*, pp. 201-203, John Wiley, New York, 1978.
Spinks, J. W. T., and R. J. Woods, *An Introduction to Radiation Chemistry*, p. 3, John Wiley, New York, 1990

P. A. Gerakines, Astro- and Solar-System Physics Program, Department of Physics, University of Alabama at Birmingham, 1300 University Boulevard, CH 310, Birmingham, AL 35294-1170, USA. (gerakines@uab.edu)

M. H. Moore, Code 691, Astrochemistry Branch, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA. (ummhm@lepvax.gsfc.nasa.gov)

R. L. Hudson, Department of Chemistry, Eckerd College, 4200 5th Avenue South, St. Petersburg, FL 33733, USA. (hudsonrl@eckerd.edu)

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