JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 98, NO. E3, PAGES 5505–5510, MARCH 25, 1993

IDENTIFICATION AND YIELD OF CARBONIC ACID AND FORMALDEHYDE IN IRRADIATED ICES

Neil DelloRusso and R. K. Khanna

Department of Chemistry and Biochemistry, University of Maryland, College Park

M. H. Moore

Goddard Space Flight Center, Greenbelt, Maryland

Abstract. Carbonic acid ($(OH)_2CO$) was tentatively identified in the infrared spectrum of a proton irradiated CO_2 + H_2O ice mixture [*Moore and Khanna*, 1991]. In this report we present additional evidence for a more definitive identification of $(OH)_2CO$ with (1) the infrared spectrum of a residue obtained by proton irradiation of CO_2 + D_2O ice mixture, and (2) the infrared spectra of solid phases of formaldehyde (H_2CO), acetone [$(CH_3)_2CO$], and dimethyl carbonate [$(OCH_3)_2CO$], which are structurally similar to $(OH)_2CO$. Infrared characteristics (peak frequencies and complex refractive indices of the compounds in point 2) are also reported. In particular, the integrated absorption coefficients for the C=O band for the compounds in point 2 do not vary by more than 20%. Based on these values, we estimate the yields of H_2CO and $(OH)_2CO$ by proton irradiation of ice mixtures. Both H_2CO and $(OH)_2CO$ are possible irradiation products of cometary and planetary ices.

Introduction

Formaldehyde (H_2CO) is one of the more abundant molecules in the interstellar medium [*Tielens*, 1989]. It was identified in Comet Halley [*Mumma and Reuter*, 1989] with a production rate a few percent of H_2O. Formaldehyde is also believed to be one of the products in radiation processed CH_3OH + H_2O and CO + H_2O [*Moore et al.*, 1991] and CO_2 + H_2O [*Pirronello et al.*, 1982] ice mixtures. Detailed spectroscopic studies of ion irradiated CO_2 + H_2O ices at 20 K showed that during slow warming several broad complex features evolved between 215 and 250 K. Spectral features of the residual film at 250 K were tentatively identified with carbonic acid [*Moore and Khanna*, 1991]. Carbonic acid has been conjectured to be a possible constituent in the high-temperature, high-pressure atmosphere of Venus [*Lewis and Grinspoon*, 1990], although the stability of $(OH)_2CO$ in this environment has not been firmly established. Gas phase reactions leading to the formation of $(OH)_2CO$ and its possible infrared detectability are not addressed in this paper. In view of the presence of CO_2 and H_2O on Mars, $(OH)_2CO$ is also a possible constituent, especially in the polar caps. For a positive identification and quantification of $(OH)_2CO$ in planetary environments, its characterization in the infrared region is highly desirable.

In this paper we discuss new data on the infrared spectra of the residual ice film obtained by warming the proton irradiated CO_2 + D_2O ice mixture along with the infrared spectra of crystalline H_2CO, $(CH_3)_2CO$, and $(OCH_3)_2CO$ which are structurally similar to $(OH)_2CO$. A comparison of the spectra of the CO_2 + H_2O residual film with those of the other compounds discussed above further supports our identification of carbonic acid.

We also list complex refractive indices of the crystalline H_2CO, $(CH_3)_2CO$, and $(OCH_3)_2CO$ obtained by an iterative Kramers-Kronig analysis of the transmission data for several ice film thicknesses. These data are applied to the spectra of irradiated CO + H_2O and CO_2 + H_2O ices to estimate the yields of H_2CO and $(OH)_2CO$ for known doses of radiation.

Experiment

Details of the sample preparation for proton irradiation and their spectral recording were given in an earlier report [*Moore and Khanna*, 1990]. Paraformaldehyde (Fisher), acetone (Baker, 99.6%), and dimethyl carbonate (Aldrich, 99%) were further purified by vacuum distillation. Thin films of these materials were deposited on a KRS5 substrate cooled to 20 K in a closed cycle cryocooler (Air Products 202). Freshly deposited films were invariably amorphous and were annealed at 100-150 K to convert to crystalline phases. The infrared spectra were recorded on Perkin-Elmer 1800 and Mattson Polaris Fourier transform infrared (FTIR) instruments. Resolution employed was 1.0 cm^{-1} in all cases. The tracings of the spectra of different species are given in Figures 1 and 2.

Discussion

Vibrational Assignments

Table 1 gives the infrared frequencies of the residues obtained by irradiation of CO_2 + H_2O and CO_2 + D_2O ice mixtures. These are now identified with $(OH)_2CO$ and $(OD)_2CO$, respectively. As previously reported [*Moore and Khanna*, 1991], the identification of the $(OH)_2CO$ with the residue was based on the resemblance of its infrared features with those of several hydrogen bonded systems; for example, carboxylic acids and bicarbonates [*Sadtler Research Laboratory*, 1976]. Additional data on the deuterated residue and comparison of the spectra of the residues with those of H_2CO, $(CH_3)_2CO$, and $(OCH_3)_2CO$ give a more definitive identification of carbonic acid. While the structures of H_2CO, $(CH_3)_2CO$, and $(OCH_3)_2CO$ have been elucidated by spectroscopic means, the only structural information on $(OH)_2CO$ is that from a quantum mechanical study [*Nguyen and Ha*, 1984] of the molecule. Consequently, in this work, complexities due to crystal field effects on the internal modes have been ignored.

The 4000-1900 cm^{-1} Region. The strong and broad absorptions in the region 3200-2600 cm^{-1} in the spectrum of the CO_2 + H_2O residue were assigned to the O-H ····O stretches. In the spectrum of the deuterated residue the corresponding O-D ····O peaks appear in the 2400-1900 cm^{-1} region (Figure 1), as expected. Stretching modes of CH_2 and

Paper number 92JE02325.
0148-0227/93/92JE-02325$05.00

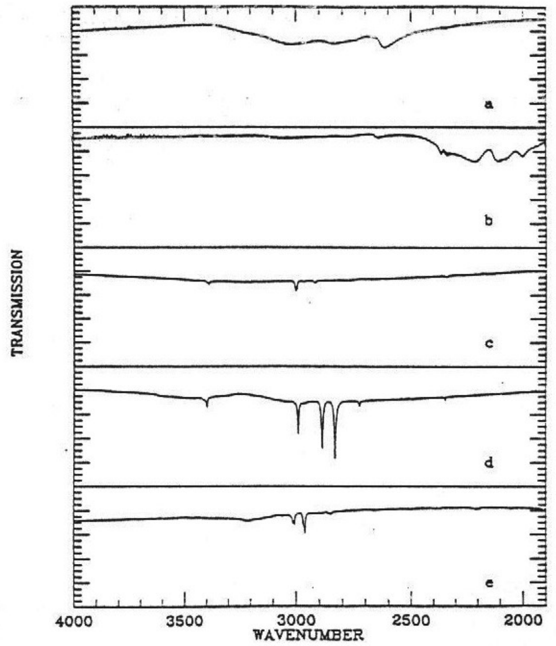

Figure 1. Infrared spectra of (a) $(OH)_2CO$, (b) $(OD)_2CO$, (c) $(CH_3)_2CO$, (d) H_2CO, and (e) $(OCH_3)_2CO$ solids in the 4000-1900 cm^{-1} region.

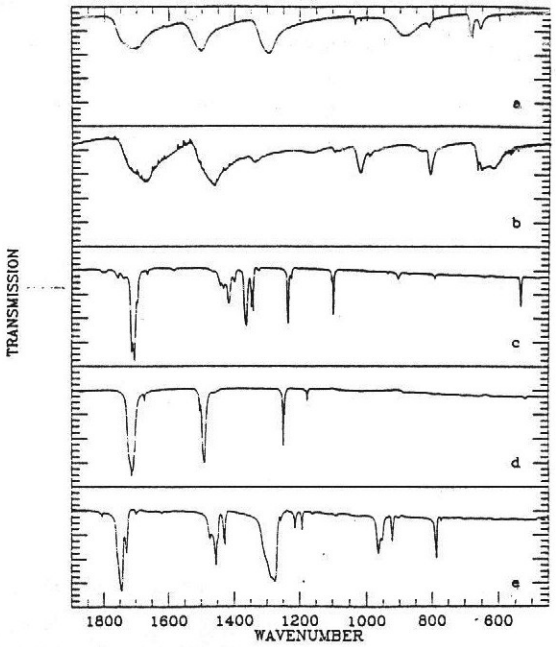

Figure 2. Infrared spectra of (a) $(OH)_2CO$, (b) $(OD)_2CO$, (c) $(CH_3)_2CO$, (d) H_2CO, and (e) $(OCH_3)_2CO$ solids in the 1900-450 cm^{-1} region.

TABLE 1. Infrared Frequencies (cm^{-1}) of Prominent Absorptions of $(H_2/D_2)CO$, $(OH/D)_2CO$, $(CH_3)_2CO$, and $(OCH_3)_2CO$ Solids

H_2O+CO_2 Residue (H_2CO_3) at 250 K	D_2O+CO_2 Residue (D_2CO_3) at 250 K	Assignment	H_2CO at 20 K	$(CH_3)_2CO$ at 20 K	$(OCH_3)_2CO$ at 20 K	Assignment
3200-2600		O-H--O st.				
			3000-2830	3000-2920	3014-2962	C-H st.
	2400-2000	O-D--O st.				
1705	1677	C=O st.	1720-1705	1714-1697	1745-1729	C=O st.
1501	1463	CO_2^* a st.				
			1505-1490	1433-1344	1473-1428	CH_2/CH_3 Bends
					1287-1278	CO_2^{**} a st.
1296		O-H--O IP				
				1260-1226	1214-1161	CH_3 Rock
			1250-1245			HCO Bend
			1179-1174			H_2CO OP
					1120	CO_2^{**} s st.
1034	997	CO_2^* s st.				
	1021	O-D--O IP				
					965-923	O-CH_3 st.
				905-793		C-$(CH_3)_2$ st.
884		O-H--O OP				
812	812	CO_3 OP				
					787	COO_2^{**} OP
					680	$OC(OCH_3)_2$ IP
	670	O-D--O OP				
682, 655	654, 621	OCO_2^* IP				
				534		$OC(CH_3)_2$ IP

Here, st = stretch; a st = asymmetric stretch; s st = symmetric stretch; OP = out of plane bend; and IP = in plane bend.
O^* = OH or OD.
O^{**} = OCH_3.

CH_3 groups in complex molecules are generally extremely sharp and occur above 2800 cm^{-1} [*Sadtler Research Laboratory*, 1976]. Even though the $CO_2 + H_2O$ residual ice film shows a relatively sharp band at 2614 cm^{-1} (1999 cm^{-1} for the corresponding band in the spectrum of the $CO_2 + D_2O$ residue), its width is approximately 3 times that of the CH stretch in hydrocarbons. The structures of the absorption features of the residues resemble those of bicarbonates and carboxilic acids. These data therefore indicate absence of CH/CD bonds in the residues discussed above.

The 1900-450 cm^{-1}.Region. Spectral traces of H_2CO, $(CH_3)_2CO$, and $(OCH_3)_2CO$ and the residual films are reproduced in Figure 2. The broad nature of the bands in the spectra of residues is possibly due to hydrogen/deuterium bonding. Somewhat sharper bands for the deuterated

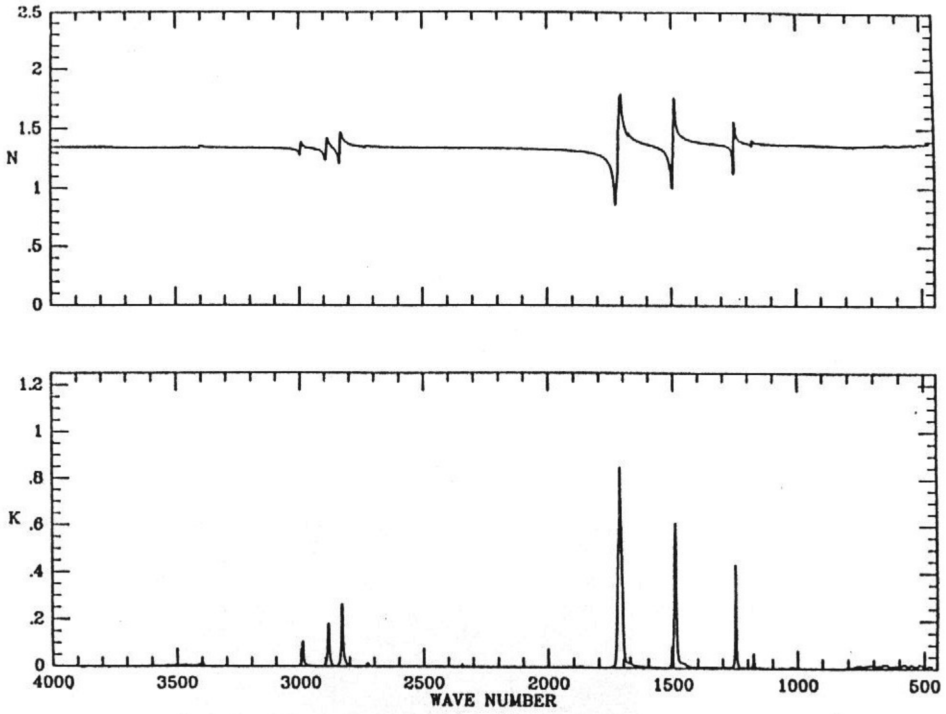

Figure 3. Plots of n and k versus v for crystalline H_2CO.

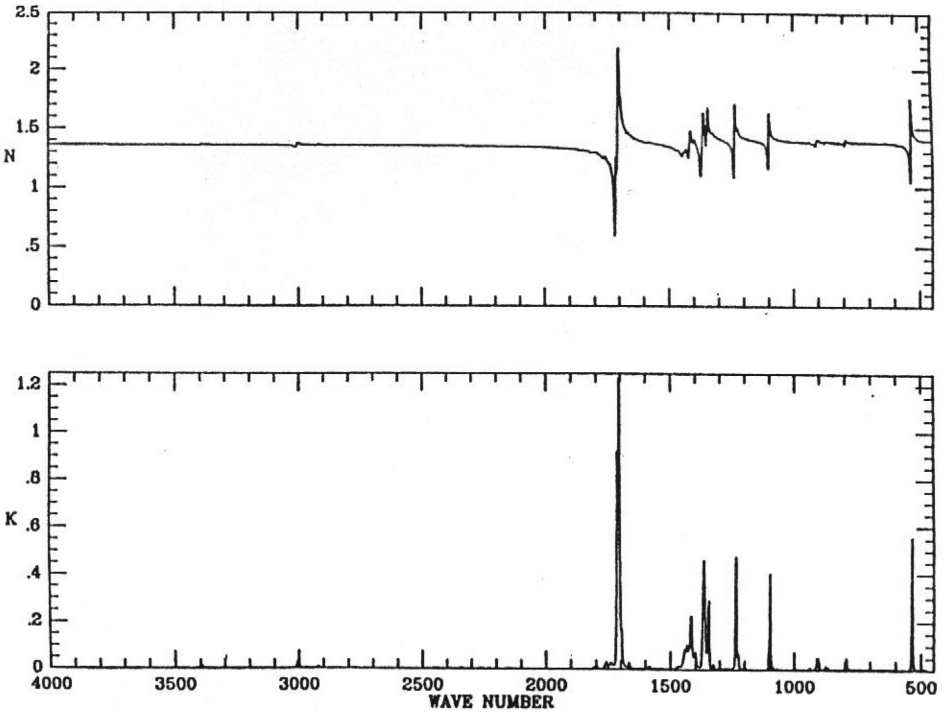

Figure 4. Plots of n and k versus v for crystalline $(CH_3)_2CO$.

samples are due to relatively smaller vibrational amplitudes of D atoms compared to those for H atoms. One of the strongest bands in this region of the spectrum of the CO_2 + H_2O residue is at ~1700 cm^{-1}, which is characteristic of a C=O bond. H_2CO, $(CH_3)_2CO$, and $(OCH_3)_2CO$ exhibit the C=O band at 1714 cm^{-1}, 1711 cm^{-1}, and 1745 cm^{-1}, respectively. The higher frequency for $(OCH_3)_2CO$ is due to charge transfer to the carbonyl group through the O atoms connected to the CH_3 group. From the structural point of view, the C=O band of $(OH)_2CO$ should be closer to that of $(OCH_3)_2CO$; however, hydrogen bonding is expected to lower the frequency. Thus the assignment of the 1705 cm^{-1} band to the C=O of the $(OH)_2CO$ is justified. A somewhat lower frequency for the C=O band of $(OD)_2CO$ is due to increased effective mass of the unit.

The bands at 1501 cm^{-1} and 1296 cm^{-1} in the spectrum of the $CO_2 + H_2O$ residue were previously assigned to O-H ....O in plane bend and $C(OH)_2$ asymmetric stretch, respectively. An apparent disagreement with the normal coordinate analysis was attributed to mixing of the two modes. On deuteration, the 1296 cm^{-1} band shifts to 1021 cm^{-1}, whereas the 1501 cm^{-1} band is only slightly shifted to 1463 cm^{-1}. In the former case the 1501 cm^{-1} and 1296 cm^{-1} bands are about equally intense due to strong mixing of the modes, whereas in the latter case the two bands are farther apart, resulting in less mixing of the modes and hence differences in their relative intensities. Crystalline H_2CO, $(CH_3)_2CO$, and $(OCH_3)_2CO$ have bands in the same vicinity (Table 1); however, those are due to CH_2/CH_3 groups (e.g., CH_2 bend: 1500 cm^{-1}, CH_3 bends: 1450 cm^{-1} and 1375 cm^{-1}, CH_3 rock: 1200 cm^{-1}). Thus the analysis of this region further supports the absence of CH/CD bonds in the residue species. Dimethyl carbonate has a strong band at 1280 cm^{-1}, which has been assigned to $(OCH_3)_2C$ asymmetric stretch [*Katon and Cohen*, 1975]; the difference in the corresponding band for $(OH)_2CO$ is due to the hydrogen bonding in the latter, which results in a mixing of the O-H ....O in plane bend and the $C(OH)_2$ asymmetric stretch.

The data on the deuterated residue confirm our assignments of the other modes of $(OH)_2CO$. Thus, the 840 cm^{-1} band, which shifts to 670 cm^{-1} on deuteration, is due to the out of plane bend of the COH group; other bands are due to the skeletal CO_3 group (810 cm^{-1}: CO_3 out of plane bend, 682 and 655 cm^{-1} doublet: CO_3 in plane bend) and are shifted only slightly on deuteration. Thus the infrared characteristics of carbonic acid are more definitively established.

Refractive Indices

The procedure for the determination of n and k from the absorption spectra of thin films of the samples has been described in detail in several previous reports from this laboratory [*Pearl et al.*, 1991; *Masterson and Khanna*, 1990]. For H_2CO, $(CH_3)_2CO$, and $(OCH_3)_2CO$ the complex refractive indices were determined by an iterative Kramers-Kronig analysis of the transmission data for several film thicknesses. Figures 3-5 give the plots of n and k for these crystalline samples. For the residue films, which did not show any interference pattern, the thickness could not be directly determined. However, it is noticed (Table 2) that the integrated extinction coefficient for the 1700 cm^{-1} bands of H_2CO, $(CH_3)_2CO$, and $(OCH_3)_2CO$ do not vary by more than 20%. The averaged value for the integrated extinction coefficient (for the three samples) was utilized to obtain the optical thickness of the residue films from their measured absorbance in the 1700 cm^{-1} region. This information was utilized to determine the product yields for given radiation doses as described below.

Product Yields

Information required for the calculation of the yield of $(OH)_2CO$ (number of $(OH)_2CO$ molecules per 100 eV absorbed) was obtained from the infrared spectra of $H_2O + CO_2$ ice before and after irradiation in six different experiments and from the measured incident 700 keV proton dose. Before irradiation an average H_2O thickness was calculated from the 3280 cm^{-1}, 1660 cm^{-1}, and 760 cm^{-1} absorptions using appropriate band intensities and absorption coefficients [*Bertie et al.*, 1969; *Wood and Roux*, 1982]. Assuming a density of 1.46 g cm^{-3}, an average CO_2 thickness was calculated from the $^{13}CO_2$ absorption using appropriate band intensities for $^{13}CO_2$ (correcting for the natural $^{13}CO_2/^{12}CO_2$ abundance ratio) and absorption coefficients for the combination lines [G.Sill, unpublished data,1992]. From this information the total physical thickness was determined. After irradiation, the equivalent thickness of $(OH)_2CO$ was determined by integrating the absorbance of the C=O band at 1700 cm^{-1} band and dividing by the estimated integrated absorption coefficient. A typical incident irradiation dose is $\sim 1\times10^{15}$ protons cm^{-2}. This value is multiplied by the stopping power (430 MeV cm^2 g^{-1}) of 700 keV protons [*Northcliffe and Shilling*, 1970]; the density of

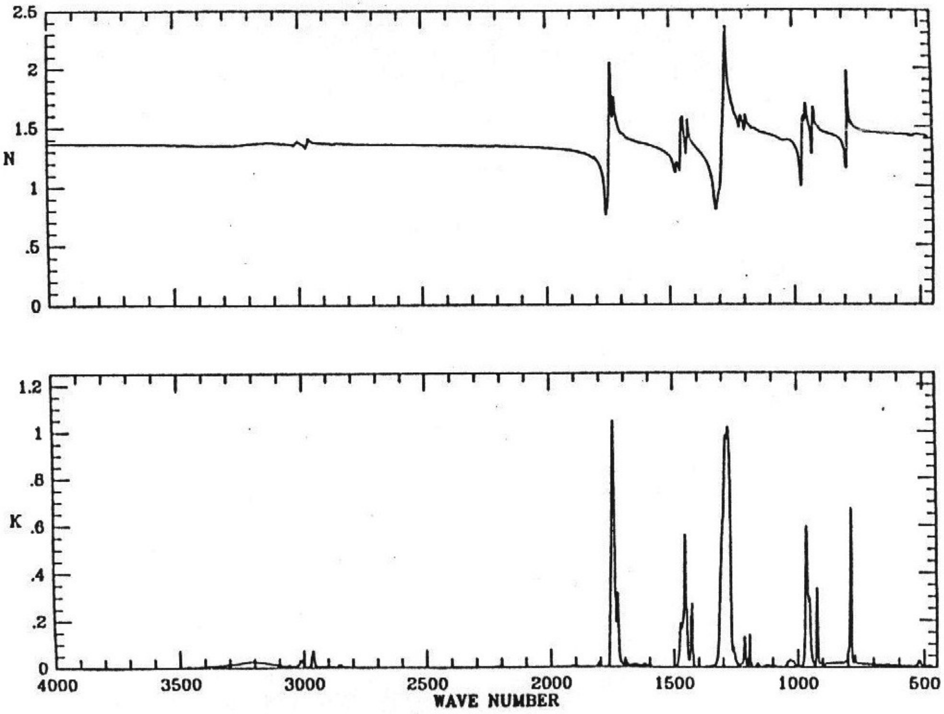

Figure 5. Plots of n and k versus ν for crystalline $(OCH_3)_2CO$.

TABLE 2. Integrated Extinction Coefficients for Some Bands of Formaldehyde, Dimethyl Carbonate, and Acetone

Integral Range, cm^{-1}	$\alpha^* = \int \alpha d\nu$ X10^4 cm^{-2}	$k^* = \int k d\nu$ cm^{-1}
	Formaldehyde	
3420-3380	0.741	0.174
3020-2940	3.41	0.908
2910-2850	6.02	1.66
2858-2790	8.70	2.45
2740-2710	0.361	0.105
1760-1600	32.3	15.0
1520-1400	14.4	7.68
1270-1225	2.93	1.87
1190-1165	0.327	0.221
	Dimethyl Carbonate	
3070-2990	2.16	0.571
2990-2870	3.52	0.950
2870-2810	0.588	0.164
1820-1590	41.6	19.0
1500-1410	19.2	10.5
1350-1240	60.2	37.2
1240-1205	1.22	0.796
1205-1175	0.830	0.555
1000-930	10.7	8.88
930-900	2.35	2.03
810-760	4.47	4.51
	Acetone	
3410-3360	0.408	0.0959
3030-2980	1.25	0.330
2980-2960	0.104	0.0279
2940-2900	0.272	0.0741
1830-1650	33.2	15.4
1500-1380	8.76	4.88
1380-1320	11.5	6.71
1260-1190	4.63	2.99
1120-1060	2.64	1.92
950-860	0.721	0.633
810-780	0.232	0.233
550-510	1.75	2.60

the ice, 1 g cm^{-3}; and the physical thickness, e.g. ~ 1 µm, to give the absorbed dose: 4.19 eV cm^{-2}. The number of $(OH)_2CO$ molecules cm^{-2} divided by the absorbed dose (eV cm^{-2}) multiplied by 100 gives the yield. An identical procedure was followed to determine the yield of H_2CO in an irradiated H_2O + CO ice. Only one experimental data set was used for this determination. The film thickness before irradiation was estimated from the known extinction coefficient for the 2140 cm^{-1} band of solid CO [*Sandford et al.*, 1988] and the density of CO (0.8 g cm^{-3}). The results are yield of $(OH)_2CO$ in H_2O+CO_2 ice: ~0.5/100 eV and yield of H_2CO in H_2O+CO ice: ~1.0/100 eV.

Implications for Cosmic Ices

On the basis of these laboratory results, irradiation of CO + H_2O and CO_2 + H_2O cosmic ice mixtures could result in significant synthesis of H_2CO and $(OH)_2CO$. For example, it has been estimated that the top layer of a comet stored 4.5x10^9 years in the Oort cloud would receive about 100-150 eV/H_2O molecule, ices at a depth of 1 m would receive about 40 eV/H_2O molecule and the center of the 20 km comet nucleus would get less than 10 eV/H_2O molecule [*Johnson*, 1991]. At the center much of the dose comes from radionuclide decay [*Draganic et al.*, 1984]. However, yields of products in more complex mixtures (three or more components) can be altered because of competing reactions. Nevertheless, the spectral patterns for H_2CO and $(OH)_2CO$ are uniquely different between 5.5 µm and 8.3 µm, a region which can be searched for these molecules in a comet nucleus (before a coma has developed) or on interstellar grains.

Another example is the planet Mars, which has an atmosphere dominated by CO_2 along with some H_2O. Since temperatures can drop below 150 K in the winter, co-deposits of these gases form in the polar caps. An estimate of the yearly cosmic ray surface dose on the surface of Mars is on the order of 10 times less than a yearly surface dose on a comet in the Oort cloud [*Simonsen et al.*, 1990]. Because of the low dose, it seems unlikely that significant amounts of $(OH)_2CO$ could be accumulated in ices that sublime each season. However, experiments more relevant to Mars are required to determine the actual vapor pressure of $(OH)_2CO$, the yield from ices irradiated at 150 K, and with different initial CO_2 : H_2O ratios.

Acknowledgment. This work was made possible by a NASA grant, NAGW-637, from the Planetary Atmospheres Program.

References

Bertie, J.E., H.J. Labbe, and E. Whalley, Absorptivity of Ice I in the range 4000-30 cm^{-1}, *J. Chem. Phys.*, *50*, 4501-4520, 1969.

Draganic, I.G., Z.D. Draganic, and S. Vujosevic, Some radiation-chemical aspects of chemistry in cometary nuclei. *Icarus*, *60*, 464-475, 1984.

Johnson, R.E., Irradiation effects in a comet's outer layers, *J. Geophys. Res.*, *96*(E2), 17,553-17,557, 1991.

Katon J.E., and M.D. Cohen, The vibrational spectra and structure of dimethyl carbonate and its conformational behavior, *Can. J. Chem.*, *53*, 1378-1386, 1975.

Lewis, J.S., and D.H. Grinspoon, Vertical distribution of water in the atmosphere of Venus: A simple thermochemical explanation, *Science*, *249*, 1273-1275, 1990.

Masterson, C.M., and R.K. Khanna, Absorption intensities and complex refractive indices of crystalline HCN, HC_3N, and C_4N_2 in the infrared region, *Icarus*, *83*, 83-92, 1990.

Moore, M.H., and R.K. Khanna, Infrared and mass spectral studies of proton irradiated $H_2O + CO_2$ ice: Evidence for carbonic acid, *Spectrochim. Acta*, *47A*, 255-262, 1991.

Moore, M.H., R.K. Khanna, and B.Donn, Studies of proton irradiated $H_2O + CO_2$ and $H_2O + CO$ ices and analysis of synthesized molecules, *J. Geophys. Res.*, *96*(E2), 17,541-17,545, 1991.

Mumma, M.J., and D.C. Reuter, On the identification of formaldehyde in Halley's comet, *Astrophys. J.*, *344*, 940-948, 1989.

Nguyen, M.T., and T. Ha, A theoretical study of the formation of carbonic acid from the hydration of carbon dioxide: A case of active solvent catalysis, J. *Am. Chem. Soc.*, *106*, 599-602, 1984.

Northcliffe, L.C., and R.F. Shilling, Range and stopping power tables for heavy ions, *Nucl. Data Tables*, *A7*, 233-263, 1970.

Pearl, J.C., M. Ngoh, M.J. Ospina, and R.K. Khanna, Optical constants of solid methane and ethane from 10,000 to 450 cm^{-1}, *J. Geophys. Res.*, *96*(E2), 17,477-17,482, 1991.

Pirronello, V., W. L. Brown, L. J. Lanzerotti, K. J. Marcantonio, and E. H. Simmons, Formaldehyde formation in a H_2O/CO_2 ice mixture under irradiation by fast ions, *Astrophys. J.*, *262*, 636-640, 1982.

Sadtler Research Laboratory, Inc., *The Sadtler Standard Spectra*, Philadelphia, 1976.

Sandford, S.A., L.J. Allamandola, A.G.G.M. Tielens, and G.J. Valero, Laboratory studies of the infrared spectral properties of CO in astrophysical ices, *Astrophys. J.*, *329*, 498-510, 1988.

Simonsen, L.C., J. E. Nealy, L. W. Townsend, and J. W. Wilson, Estimate of radiation dose on the surface of Mars, *J. Spacecraft*, *27*, 353-354, 1990.

Tielens, A.G.G.M., Interstellar dust, in Proceedings, IAU Symposium, *135*, edited by. L.J. Allamandola, and A.G.G.M. Tielens, 239-262, International Astronomical Union, 1989.

Wood, B.E., and J.A. Roux, Infrared optical properties of thin H_2O, NH_3, and CO_2 cryofilms, *J. Opt. Soc. Am.*, *72*, 720-728, 1982.

N. DelloRusso and R.K. Khanna, Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742.

M.H. Moore, Goddard Space Flight Center, Greenbelt, MD 20771.

(Received February 10, 1992;
revised August 28, 1992;
accepted October 1, 1992.)