JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 96, NO. E2, PAGES 17,541-17,545, SEPTEMBER 25, 1991

Studies of Proton Irradiated H_2O+CO_2 and H_2O+CO Ices and Analysis of Synthesized Molecules

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Infrared spectra of H_2O+CO_2 and H_2O+CO ices before and after proton irradiation showed that a major reaction in both mixtures was the interconversion of $CO_2 \rightleftharpoons CO$. Radiation synthesized organic compounds such as carbonic acid were identified in the H_2O+CO_2 ice. Different chemical pathways dominate in the H_2O+CO ice in which formaldehyde, methanol, ethanol, and methane were identified. Sublimed material was also analyzed using a mass spectrometer. Implications of these results are discussed in reference to comets.

INTRODUCTION

Formaldehyde, H_2CO, is one of the interstellar molecules with the highest relative abundance (approximately 0.3% that of H_2O [*Guelin*, 1984]). It may condense onto interstellar grains and become incorporated into any comets formed from these materials. Cometary H_2CO was first detected in comet Halley with a production rate a few percent of that of H_2O. Emissions were detected in the radio [*Snyder et al.*, 1989] and in the infrared spectral region [*Moroz et al.*, 1987; *Combes et al.* 1986; *Knacke et al.*, 1986; *Dankes et al.*, 1987].

Radiation processing (photolysis and/or particle radiation) of interstellar icy materials such as H_2O, CH_4, CO, CO_2, and CH_3OH may result in the synthesis of H_2CO increasing its abundance. Therefore pathways leading to the synthesis of H_2CO have been examined in several laboratory experiments.

Results from several photolysis experiments showed the synthesis of H_2CO in icy mixtures containing H_2O and CO along with other molecules [e.g., *Greenberg*, 1982; *d'Hendecourt et al.* 1986; *Allamandola et al.*, 1988]. More recently, *Zhao* [1990] reported the detection of H_2CO in both photolyzed H_2O+CO_2 and H_2O+CO. There have been two reports of the detection of H_2CO from ion irradiated H_2O+CO_2; one experiment used mass spectroscopy [*Pirronello et al.*, 1982] and one used infrared spectroscopy [*Rocard*, 1986].

We have examined the infrared spectrum of H_2O+CO_2 and H_2O+CO before and after irradiation and have identified most species synthesized in the ice. The evolution of spectra during warming was observed, along with the mass spectral detection of species released during vaporization. We compare and contrast irradiation results of these two icy mixtures.

EXPERIMENTAL PROCEDURES

Thin ice films were formed by condensing gas mixtures of H_2O+CO_2 or H_2O+CO onto an aluminum mirror (T=20 K) attached to the tail section of a closed-cycle cryostat. One window of the cryostat was directed to a reflection attachment on a Mattson Polaris FT-IR (Fourier Transform Infrared) spectrometer another was connected to a Dycor (model M200M) quadrupole mass spectrometer, and a third was connected to a Van de Graaff accelerator. The ice sample could be rotated to face one of these ports depending on the nature of the experiment: spectroscopy, vaporization, or irradiation. Details of this experimental setup are given by *Moore et al.* [1988].

RESULTS

The infrared spectrum from 4000 to 400 cm^{-1} of an ~6µm-thick H_2O+CO_2 (~1.4:1) ice is shown in Figure 1. The absorptions of H_2O and CO_2 in the newly deposited ice are labeled in Figure 1*a*. After irradiation (Figure 1*b*) many new features appear in the spectrum. The sharp feature at 2143 cm^{-1} is identified as ^{12}CO and that at 2094 cm^{-1} as ^{13}CO. Tentative identification of carbon suboxide, C_3O_2, is at 2237 cm^{-1} [*Miller and Fateley*, 1964; V.G. Anicich and M. Allen, private communication, 1991] . CO_3 radical species could be associated with the weak features at 2044 and 1878 cm^{-1} [*Jacox et al.*, 1971]. Figure 1*b* "expanded" (lowest spectrum in lower box) shows a more detailed view of the irradiated sample, between 1800 and 900 cm^{-1}. There is some similarity between positions of the synthesized features at 1714, 1482 and 1294 cm^{-1} and the positions of formaldehyde absorptions ($\tilde{\nu}_2$, $\tilde{\nu}_3$, and $\tilde{\nu}_6$) in an H_2O+H_2CO ice (see Figure 2*c*). However, we believe this similarity is not evidence for the presence of H_2CO because there are differences between the relative intensities, positions, and bandwidths of the peaks in the irradiated ice and those of H_2CO. We observed that when irradiated H_2O+CO_2 was warmed slowly to 250 K, the ice evolved into a film whose absorptions were identified as carbonic acid, H_2CO_3 [*Moore and Khanna*, 1991]. There are

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Paper number 91JE01682.
0148-0227/91/91JE-01682$05.00

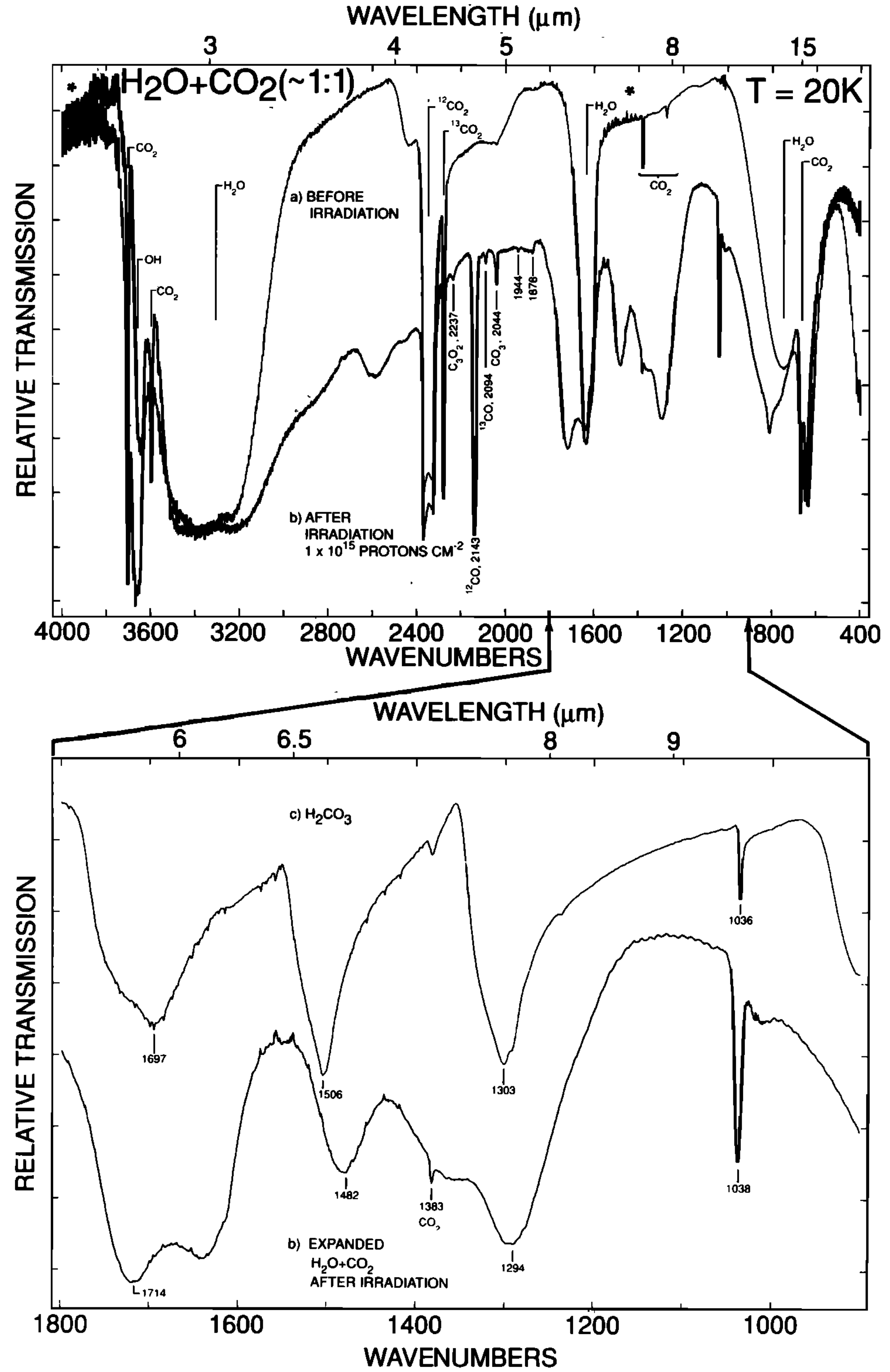

Fig. 1. The infrared spectrum from 4000 to 400cm^{-1} of an ~6μm-thick H_2O+CO_2 (~1.4:1) ice is shown (*a*) before and (*b*) after proton irradiation. Figure 1*b* expanded is a detailed look at the irradiated spectrum between 1800 and 900cm^{-1}. Figure 1*c* is similar to the irradiated ice and resulted from freeze drying irradiated H_2O+CO_2. It was produced in our laboratory and identified [*Moore and Khanna,* 1991] as carbonic acid. Regions with structure due to apparent errors in ratioing are marked with an asterisk.

many similarities between the spectrum of irradiated H_2O+CO_2 at 20 K and the spectrum of H_2CO_3 recooled to 20 K (shown in Figure 1*c*). This correspondence suggests that H_2CO_3 forms directly during irradiation not just as a product of the thermal evolution.

Most H_2CO_3 (mass 62) dissociates into CO_2 (mass 44) and H_2O (mass 18) during vaporization and these masses, but not mass 62, were detected in the mass spectrometer during warming. Using different isotopic mixtures containing, e.g., D_2O, $^{13}CO_2$ we confirmed that masses 30 or 29 (attributed to

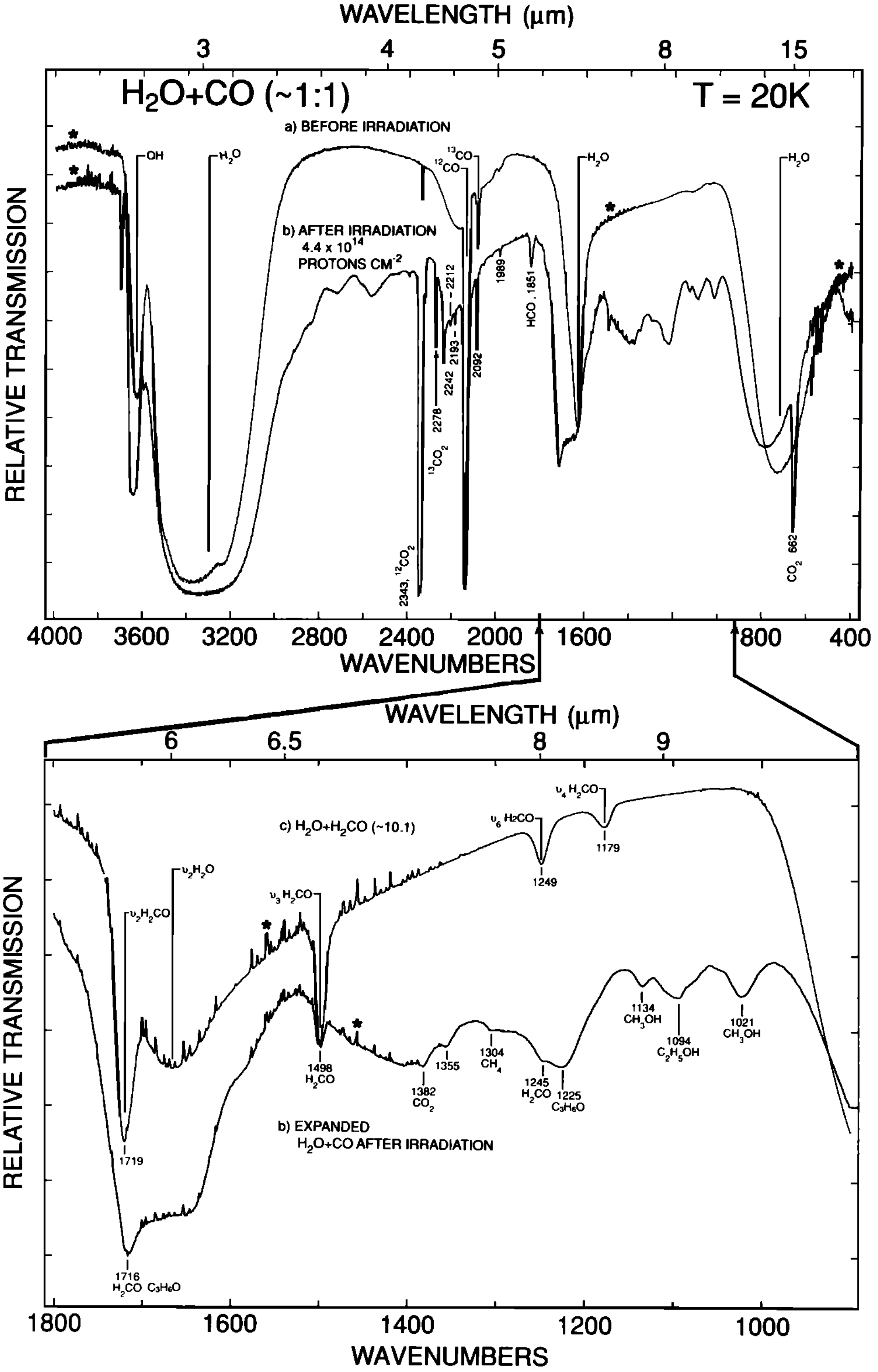

Fig. 2. The infrared spectrum from 4000 to 400cm⁻¹ of an ~3μm-thick H_2O+CO ice(~1:1) is shown (*a*) before and (*b*) after proton irradiation. Figure 2*b* expanded is a detailed look at the irradiated ice between 1800 and 900cm⁻¹. Absorptions of synthesized molecules are identified. The detection of H_2CO is based on similarities with Figure 2*c*, the spectrum of H_2O+H_2CO. Regions with structure due to apparent errors in ratioing are marked with an asterisk.

H_2CO or HCO) were also detected between 110 K and 250 K. Some H_2CO therefore exists in the ice, but its association with carbonic acid which appears to dominate the infrared spectrum is not clear.

The infrared spectrum from 4000 to 400 cm⁻¹ of an ~3μm thick H_2O+CO ice (~1:1) is shown in Figure 2. The absorptions of H_2O and CO in the newly deposited film are labeled. After irradiation (Figure 2*b*) many new features appear in the spectrum. The sharp line at 2343 cm⁻¹ is due to $^{12}CO_2$ and that at 2278 cm⁻¹ to $^{13}CO_2$. The weak absorption at 1851 cm⁻¹ is attributed to HCO [*Milligan and Jacox*, 1964], and possible candidates for the 2242 and 1989 cm⁻¹ absorptions are C_3O_2 and C_2O [*Jacox and Milligan*, 1965] respectively. At 250 K essentially no residual film remains from this irradiated ice; no formaldehyde polymer was detected. Figure 2*b* "expanded" (lowest spectrum in lower box) shows spectral details of the irradiated sample between 1800 and 900 cm^{-1}. The similarities between positions of the synthesized features at 1716, 1498 and 1245 cm^{-1} and the ν_2, ν_3, and ν_6 absorptions of H_2CO in H_2O (Figure 2*c*) support the identification of H_2CO in this ice. The ratio of the integrated absorbance of the 1716 and 1498 cm^{-1} peaks in the irradiated ice (bands were deconvolved using standard curve fitting programs) was larger than the corresponding ratio for the H_2O+H_2CO ice in Figure 2*c*. This suggests that other C=O bonded molecules are contributing to the 1716 cm^{-1} line; a possible candidate is acetone which also has an absorption near 1225 cm^{-1}. CH_4, methanol (CH_3OH), and ethanol (C_2H_5OH) were identified by comparison with spectra of proton irradiated pure CH_3OH and CH_3OH+H_2O (new molecules synthesized were C_2H_5OH, H_2CO, CH_4, CO, CO_2 (M. H. Moore et al., manuscript in preparation, 1991)).

Mass 30 was detected with a mass spectrometer during warming from 40 K to near 200 K and was attributed to H_2CO. The detection of mass 68 at 43 K, at 54 K, and from 160 K to near 200 K was attributed to C_3O_2.

DISCUSSION

The original motivation for our proton irradiation studies of H_2O+CO_2 and H_2O+CO was to confirm earlier reports of the synthesis of H_2CO in each of these mixtures. We found that the common reaction in the spectra of both ices after irradiation was the interconversion of $CO_2 \rightleftharpoons CO$; in H_2O+CO_2, $CO_2 \rightarrow CO$ (the CO_2/CO ratio decreases) and in H_2O+CO, $CO \rightarrow CO_2$ (the CO/CO_2 ratio decreases). The differences between these two ices were greatest in the 1800-900 cm^{-1} region, suggesting that other reactions occur with different dominant chemical pathways.

We have identified H_2CO_3 in the infrared spectrum of irradiated H_2O+CO_2 but were unable to identify H_2CO. This result is consistent with the expected yield of H_2CO (calculated using mass spectral data from *Pirronello et al.* [1982]) which would result in intensities of H_2CO too small to be detected in our infrared spectra. Our detection of mass 30 in the mass spectrometer during warming may be due to H_2CO, consistent with the studies of *Pirronello et al.*[1982]. Previous identifications of H_2CO in processed H_2O+CO_2 ices relied on the 1714 cm^{-1} line as a strong indication that H_2CO was present, but this line is also present in the carbonic acid spectrum (both molecules have a C=O stretch).

Both infrared and mass spectrometer data support the identification of H_2CO in irradiated H_2O+CO ices consistent with the photolysis results on similar ices [*Greenberg*, 1982; *d'Hendecourt et al.*, 1986; *Allamandola et al.*, 1988; *Zhao*, 1990]. Other spectral features in the irradiated spectrum have been identified as CH_3OH, C_2H_5OH, and CH_4 based on our preliminary studies of CH_3OH irradiation. However, neither the reaction rates nor the chemical pathways for $H_2O+CO \rightarrow H_2CO$, CH_3OH, CH_4, and C_2H_5OH are known. In pure CH_3OH, the H_2CO/CH_3OH and CH_4/CH_3OH ratios increase with radiation processing (M. H. Moore et al., manuscript in preparation, 1991) but this may be different in icy mixtures or depend on whether CH_3OH is present or synthesized in the ice.

This laboratory work suggests that the abundances of CO, CO_2, CH_3OH, CH_4, and H_2CO in radiation processed ices will be different from unaltered interstellar ices. Ratios such as CO_2/CO and H_2CO/CH_3OH can be used as an indicator of processing prior to accretion into comets if the differences apply to both dynamically old and new comets. Particle radiation processing after accretion would be enhanced in the outer region of a nucleus compared to the interior. This would cause differences in molecular ratios between old and new comets. The significance of any carbonic acid in comets may lie in the possibility that icy grains could transport it into the coma where it would dissociate into H_2O and CO_2. Currently, the determination of the CO_2/CO ratio in H_2O+CO_2 and H_2O+CO ices processed until $CO_2 \rightleftharpoons CO$ equilibrium is reached is in progress (M. H. Moore et al., manuscript in preparation, 1991). Further laboratory studies will investigate the interrelationship between H_2CO, CH_3OH and CH_4.

Acknowledgments. The authors thank members of the Radiation Facility at NASA GSFC for operation of the accelerator. This work was supported by NASA grants NSG5-172 and NAGW-637. This work was completed at NASA GSFC.

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(Received February 15,1991;
revised May 13, 1991;
accepted May 13, 1991.)