

EFFICIENT FORMATION OF FORMALDEHYDE AND METHANOL BY THE ADDITION OF HYDROGEN ATOMS TO CO IN H₂O-CO ICE AT 10 K

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ABSTRACT

Formaldehyde and methanol were produced efficiently by the hydrogenation of CO in H₂O-CO ice at 10 K in an atomic hydrogen beam experiment. The relative yields to the initial CO were of the order of 10%, 3 orders of magnitude larger than those reported previously. This reveals for the first time experimentally that successive hydrogenation of CO is most likely to produce formaldehyde and methanol on the surface of icy grains in molecular clouds as suggested by theoretical models.

Subject headings: dust, extinction — ISM: molecules — methods: laboratory — molecular data — molecular processes

1. INTRODUCTION

Simple organic molecules, formaldehyde (H₂CO) and methanol (CH₃OH), were found in some comets (e.g., Crovisier & Bockelée-Morvan 1999) and interstellar ices (e.g., Keane et al. 2001). Gas-phase reactions (e.g., Shalabiea & Greenberg 1994) and UV photolysis of H₂O-CO ice (Allamandola, Sandford, & Valero 1988; Schutte et al. 1996) are insufficient to explain the observed abundances in interstellar ices. A proton bombardment experiment by Hudson & Moore (1999) demonstrated yields of H₂CO and CH₃OH from H₂O-CO ice of up to 7% and 12%, respectively. In over 4.6 billion years, this process would be effective in producing methanol in the comet's nucleus.

In theoretical models, the successive hydrogenation of CO on an ice surface, CO → HCO → H₂CO → CH₃O → CH₃OH, was proposed to produce H₂CO and CH₃OH (e.g., Tielens & Whittet 1997; Charnley, Tielens, & Rodgers 1997). In this context, Hiraoka et al. (1994) sprayed cold H atoms onto solid CO at 13 K and observed H₂CO and CH₃OH in low yields of the order of 0.01% in temperature-programmed desorption (TPD) spectra. Furthermore, they recently reported that no CH₃OH was detected as the product of CO hydrogenation (Hiraoka & Sato 2001). Unfortunately, quantitative information such as the relation between the yields and the H dose was not clear in their experiments. To clarify the role of H atoms in the formation of H₂CO and CH₃OH quantitatively, we measured the yields of these molecules formed by the H addition to CO in a H₂O-CO ice at 10 K with the Fourier transform infrared spectrometer (FTIR) and temperature-programmed thermal desorption.

2. EXPERIMENTAL

The experimental apparatus is shown in Figure 1. The apparatus consists of a main chamber and a differentially pumped atomic source chamber. A cryogenic aluminum substrate is located in the center of the main chamber and surrounded by a large copper shroud connected to a liquid-nitrogen reservoir. Base pressures were beginning at 10⁻¹⁰ torr in the main chamber and at mid-10⁻⁸ torr in the atomic source chamber. Atomic hydrogen was produced by the dissociation of H₂ molecules in microwave plasma in a water-cooled Pyrex discharge tube surrounded by a slotted-line microwave radiator (McCullough et al. 1993). The typical power of the microwave (2.45 GHz) fed into the radiator was 100 W with losses of several percent. It

has been reported that the dissociation fraction of this type of atomic source grows to 90% for hydrogen gas at a source pressure of 0.2 torr (McCullough et al. 1993). The Pyrex tube has a snakelike nose outlet to prevent ions and UV photons of the plasma from reaching the substrate. After the nose, a series of polytetrafluoroethylene (PTFE) tubes leads the atomic hydrogen into the main chamber. There is a 3 mm gap between the PTFE tubes in the middle of the atomic source chamber to reduce the beam flux. Two different temperatures of the hydrogen atoms were used, 300 K (warm H beam) and 80 K (cold H beam). The cold H beam was produced by adding an aluminum pipe (5 cm long with an inner diameter of 3 mm) cooled by liquid nitrogen on the end of the PTFE tube. The recombination of H atoms is suppressed on the aluminum surface at a low temperature (Koch & Steffens 1999). In the warm H-beam experiment (WHE), the aluminum pipe was removed. We measured the intensity of the warm H beam, including H₂ molecules, by using a quadrupole mass spectrometer (QMS) with a Faraday cup. In this measurement, the QMS was opposed to the atomic source in line as shown in Figure 1. The ion source of the QMS has a hole on the top so that the Faraday cup is in sight of the atomic-source direction. The beam (H+H₂) flux was estimated to be mid-10¹⁵ cm⁻² s⁻¹ for the source pressure of 0.25 torr. Typical H₂ intensities in the QMS during the microwave cycle are shown in Figure 2. The decrease in intensity during the microwave operation corresponds to the dissociation of H₂. The dissociation fraction obtained was about 10%. In the present experiment, the beam intensity was high enough to increase the pressure in the main chamber to the 10⁻⁷ torr range because of a large number of H₂ molecules formed by H-H recombination on the wall of the chamber (i.e., background H₂). The QMS not only detects molecules directly from the atomic source but also the background H₂. In fact, the contribution of the background H₂ to the H₂ intensity measured by the QMS was found to be the same order in magnitude as that of the atomic beam. Therefore, we believe that the dissociation fraction of 10% is a lower limit.

Amorphous H₂O-CO ice was deposited through a capillary plate located 6 cm from the 10 K substrate with an incident angle of 60°. The ratio of CO to H₂O was approximately 0.2. Ice thickness was estimated to be 120 Å. During the irradiation of H atoms at 10 K, the infrared absorption spectra were measured in situ using the FTIR (PerkinElmer, Spectrum One) with a

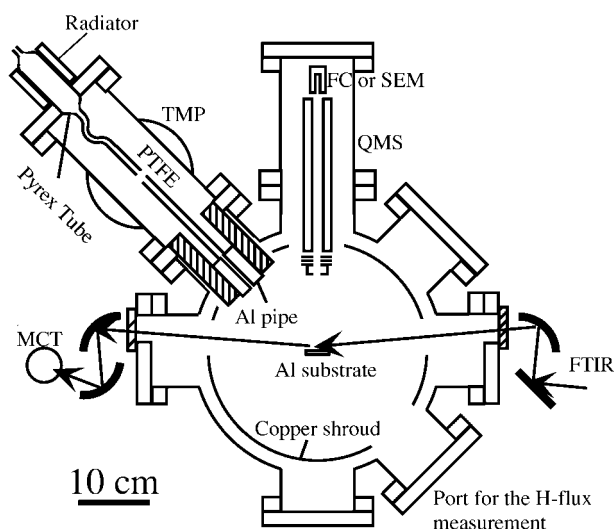


FIG. 1.—Diagram of experimental apparatus

resolution of 4 cm^{-1} . The ion gauge and QMS were off during the irradiation in order to eliminate their interference. In fact, we found that a significant number of H atoms created on a filament of the ion gauge can reach the sample substrate because of the small distance. After the irradiation, temperature-programmed mass spectra of the ice sample were measured at a rate of 5 K minute^{-1} .

3. RESULTS AND DISCUSSION

3.1. The Warm H-Beam Experiment

3.1.1. FTIR Measurements

A typical absorption spectrum of an ice sample before H irradiation is shown in Figure 3. Figure 4 shows the changes in absorption spectra after H irradiation at 10 K, which represent the absorbance variations, ΔAbs , from the initial spectrum of ice. Peaks appearing above and below the baseline indicate an increase and decrease in absorbance, respectively. As CO (2142 cm^{-1}) decreases, H_2CO appears immediately at 1722, 1499, 1249, 1178, 2991, 2887, and 2832 cm^{-1} together with CH_3OH at around 1032, 1118, and 2958 cm^{-1} . The production of small amounts of CO_2 was observed, implying the presence of a more complex surface reaction than the simple hydrogenation. However, we will concentrate our discussion on the formation of H_2CO and CH_3OH . Only a few percent of

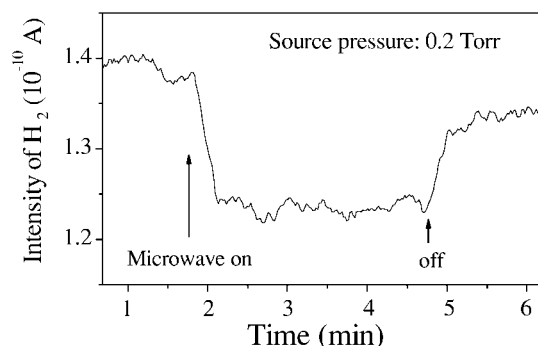
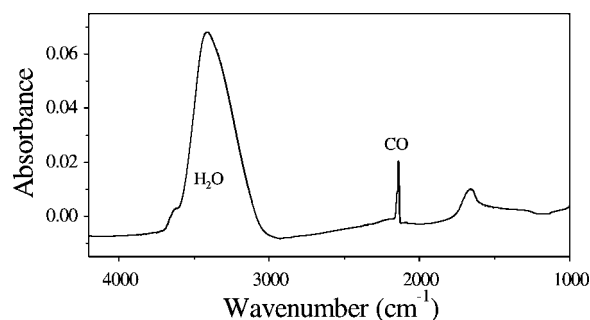


FIG. 2.—Readings from the QMS with the Faraday cup for H_2 molecules. The microwave for the atomic source was turned on at the time indicated by an arrow.

FIG. 3.—IR absorption spectrum of the initial H_2O -CO ice

CO molecules desorbed during H_2 irradiation, even without the microwave. Thus, the decrease of CO results mainly from the reaction with H atoms. The intensity of H_2CO rapidly reaches maximum at an irradiation time of about 6 minutes and then decreases gradually. Methanol increases at a slower rate than H_2CO . No intermediates such as HCO , CH_3O , and CH_2OH were observed. It should be noted that HCO has not been observed in interstellar ices. These data suggest that the rates of $\text{H} + \text{CO} \rightarrow \text{HCO}$ and $\text{H}_2\text{CO} + \text{H} \rightarrow \text{CH}_3\text{O}$ are much slower than those of $\text{H} + \text{HCO} \rightarrow \text{H}_2\text{CO}$ and $\text{CH}_3\text{O} + \text{H} \rightarrow \text{CH}_3\text{OH}$, respectively, because of relatively higher activation energies. Furthermore, in our experiment, the H flux is large enough to immediately produce the successive hydrogenation of HCO and CH_3O (or CH_2OH). Figure 5 shows a plot of the variations in area intensities (absorbances) of the main peaks for CO (2142 cm^{-1}), H_2CO (1722 cm^{-1}), and CH_3OH (1032 cm^{-1}) with H-irradiation time. Assuming an H flux of $2 \times 10^{15}\text{ cm}^{-2}\text{ s}^{-1}$ corresponding to a dissociation fraction of about 50%, the H dose is presented in the upper axis. It should be noted that the actual H dose must be somewhat lower because some fraction of H atoms is immediately expended for the H-H recombination on the surface. The intensities are normalized by the initial (nonirradiated) absorbance of CO. The CO plots become negative as CO decreases. The CO abundance almost stops de-

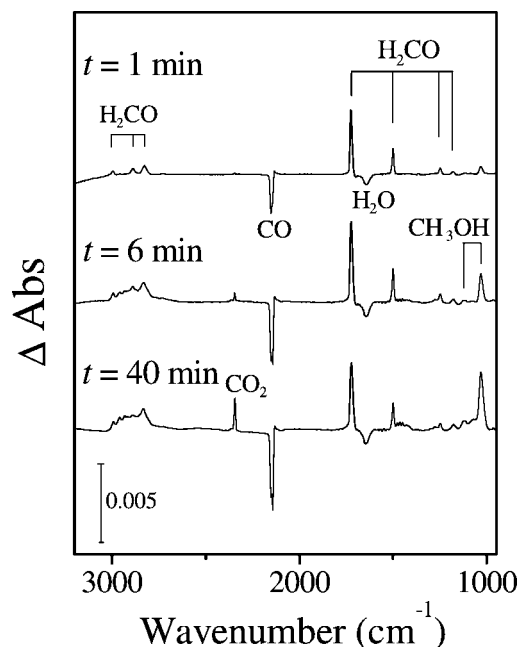


FIG. 4.—Changes in the IR absorption spectra with irradiation time of warm H atoms, minus the spectrum of the initial H_2O -CO ice (see Fig. 3).

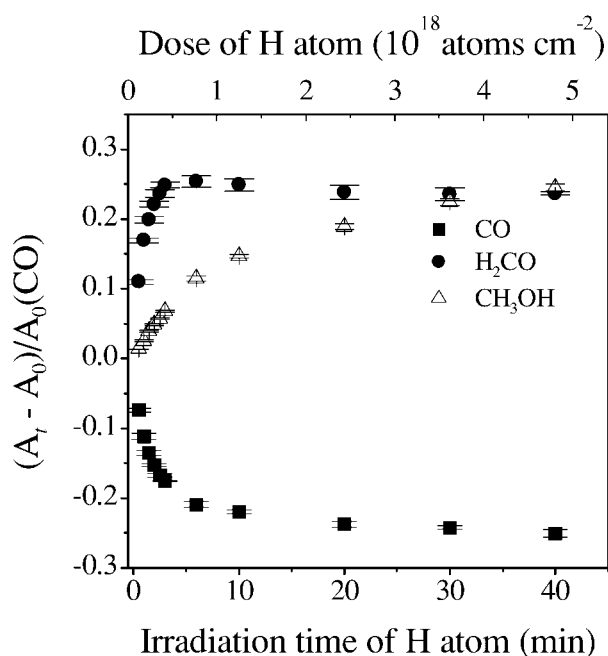


FIG. 5.—Variations in integrated absorbances for CO, H_2CO , and CH_3OH as a function of the dose of warm H atoms (*upper axis*) on the assumption of an H flux of $2 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ and the irradiation time (*lower axis*). Intensities are normalized by the absorbance of the initial CO (no H irradiation). Error bars represent the statistical error.

creasing at approximately the 20 minute irradiation. The amount of CO is finally depleted by about 25%. This value remains largely unchanged for ice thicknesses from 50 to 120 Å. These results indicate that H atoms diffuse rapidly and react with the CO in ice. The reason for the saturation of CO depletion is not clear. It may be due to CO reformation from HCO by the abstraction reaction of H. In order to estimate column densities, we applied integrated absorption coefficients 1.1×10^{-17} , 9.6×10^{-18} , and $1.6 \times 10^{-17} \text{ cm molecules}^{-1}$ for CO (Gerakines et al. 1995), H_2CO (Schutte, Allamandola, & Sandford 1993), and CH_3OH (Kerkhof, Schutte, & Ehrenfreund 1999), respectively. While the initial column density of CO is $3.2 \times 10^{16} \text{ cm}^{-2}$, the column densities after a 40 minute irradiation are $8.0 \times 10^{15} \text{ cm}^{-2}$, $8.7 \times 10^{15} \text{ cm}^{-2}$ (yield of 27% relative to the initial CO), and $5.5 \times 10^{15} \text{ cm}^{-2}$ (17%) for the CO depletion, H_2CO , and CH_3OH , respectively. However, the sum of column densities of H_2CO and CH_3OH becomes 1.8 times larger than that of the CO depletion in this attempt. It has to be smaller than the CO depletion because H_2CO and CH_3OH both originate from the CO molecule. This discrepancy may be due to errors in the estimates of the integrated absorption coefficients. However, it is still reasonable to consider that the orders of absorption coefficients for these molecules are comparable. Therefore, we conclude that about 25% of the initial CO is expended mainly to produce H_2CO and CH_3OH . Yields of H_2CO and CH_3OH relative to the initial CO are of the order of 10%. Moreover, formation of CH_3OH is as efficient as that of H_2CO . Our derived efficiencies of H_2CO and CH_3OH formation are significantly larger than those obtained in previous experiments (Hudson & Moore 1999; Hiraoka et al. 1994; Allamandola et al. 1988).

The influence of H_2 molecules on ice on the diffusion of H atoms must be considered. A large number of H_2 molecules from both the background and the atomic source may cover

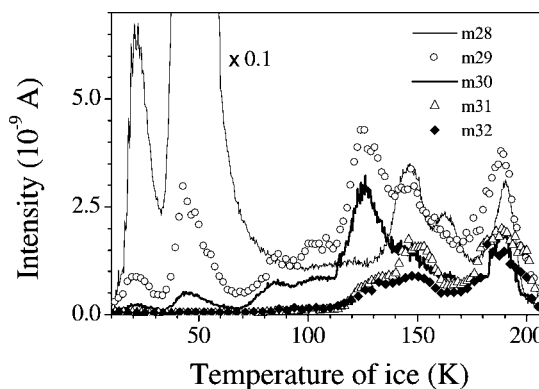


FIG. 6.—TPD spectra after 40 minutes of warm H irradiation. The intensity of a mass of 28 is reduced by 1 order of magnitude.

the ice surface. To determine any influence, we first deposited only H_2 molecules from the atomic source on ice without the microwave for 40 minutes and then turned on the microwave to produce H atoms for 40 minutes. The results are consistent with those described above, indicating that the presence of H_2 molecules on the ice surface does not significantly affect the H diffusion. Additionally, when we applied 50 V to the Al substrate to investigate the effects of ions and electrons, no changes were observed. We also examined the speed of the reaction. If it is a very slow reaction, of the order of several minutes, the abundance of molecules can change even after the H irradiation ends. No change in the abundance was observed for up to 40 minutes after the 1 minute irradiation. As a result, we conclude that the deposited H atoms react very rapidly.

3.1.2. Temperature-programmed Desorption Measurements

The TPD spectra were obtained after a 40 minute irradiation of H atoms with the QMS as shown in Figure 6. The total intensity of CO molecules was obtained by subtracting contributions of residual N_2 from the integrated intensity of mass 28 in the TPD spectra. Spectra of H_2CO molecules show peaks at masses of 29 and 30 with an $m(30)/m(29)$ ratio of approximately 0.89. The CH_3OH molecules appear at masses of 29, 31, and 32 with an $m(29)/m(31)/m(32)$ ratio of 0.65/1/0.67. Taking into account the fragmentation patterns of these molecules, the contributions of C^{18}O and ^{13}CO isotopes, and the detection efficiencies, we estimate yields of H_2CO and CH_3OH to be about 6% and 4% of the initial amount of CO, respectively. These values are somewhat smaller than those obtained by FTIR measurements. This discrepancy may be due to errors in the estimates of the integrated absorption coefficients and/or to desorption of hydrogenated products of CO during the H irradiation. Our estimated yields are considerably larger than those of $\sim 0.01\%$ for pure CO ice reported by Hiraoka et al. (1994) and Hiraoka & Sato (2001). We repeated the same measurements at 10 K using pure CO ice (results not reported here), which are consistent with the present results. The reason for the large difference between our results and those of Hiraoka et al. is not clear. Since their recent atomic source (Hiraoka & Sato 2001) has a device to eliminate photons and charged particles from the H spray, energetic processes inducing the destruction of the products do not occur in their recent experiment. Therefore, to explain the difference, we deduce that their flux of H spray is much smaller than ours. Unfortunately, they have not measured the H flux.

3.2. The Cold H-Beam Experiment

Using 80 K hydrogen atoms, we performed the same measurements as describe above. In this experiment, the intensity of the atomic beam was not recorded. The obtained IR absorption spectra are consistent with those found in the WHE. In the same manner as described in § 3.1.1, the variations of absorbances for CO, H_2CO , and CH_3OH were plotted against H-irradiation time in Figure 7. Although changes in the absorbances with irradiation time are slower than those for the WHE, the profiles of the plots are very similar. Furthermore, the depletion of CO and the yields of H_2CO and CH_3OH almost reach the same values as obtained in the WHE. We believe that the reduced rate of change is due to the relatively lower flux of the cold H beam instead of to a difference in the reaction mechanism. Adding the cold aluminum pipe to the H-beam line would lead to the decrease of the H flux.

4. ASTROPHYSICAL IMPLICATION

Our estimated yields of H_2CO and CH_3OH range from 6% to 27% and from 4% to 17%, respectively, after the H dose of $4.8 \times 10^{18} \text{ cm}^{-2}$. The upper limits are derived from the FTIR measurements, and the lower limits from the TPD spectra. These values are reasonable when compared with the observed abundances in objects toward high-mass protostars (e.g., Keane et al. 2001). Assuming that the number density of the hydrogen atom is 10 cm^{-3} and $T = 100 \text{ K}$ in a molecular cloud, the dose over 10^5 yr is about $3 \times 10^{18} \text{ cm}^{-2}$, which is comparable to our results. Although the total dose of H atoms in molecular clouds depends on the density of H atoms and the cloud's age, it is obvious that the formation of H_2CO and CH_3OH proceeds very efficiently by H-atom addition to CO in molecular clouds. When considering the physical conditions in a molecular cloud, H-atom addition will be the dominant process, as compared with the energetic processes (Hudson & Moore 1999; Allamandola et al. 1988). In the region of high-mass protostars, the CO molecule in ice would convert mainly to H_2CO and

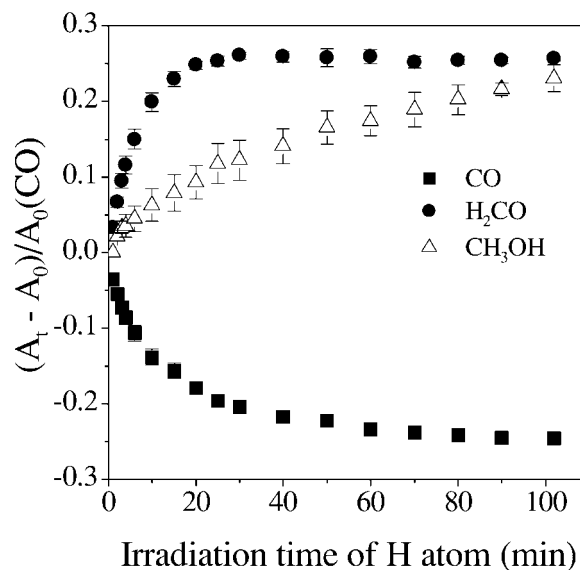


FIG. 7.—Variations in integrated absorbances for CO, H_2CO , and CH_3OH as a function of irradiation time of the cold H atoms. Intensities are normalized by the absorbance of the initial CO. Error bars represent the statistical error.

CH_3OH , or to CO_2 produced by photolysis of H_2O -CO ice or a CO+O reaction. It will be informative to simulate the evolution of CO molecules in ice by using the present results and photolysis data (Watanabe & Kouchi 2002) after acquiring the quantitative data for CO+O.

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