# CONVERSION OF H₂CO TO CH₃OH BY REACTIONS OF COLD ATOMIC HYDROGEN ON ICE SURFACES BELOW 20 K

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## ABSTRACT

The conversion of formaldehyde ($H_2CO$) to methanol ($CH_3OH$) by successive hydrogenation on $H_2O$ ice was measured at 10, 15, and 20 K using atomic hydrogen beams of 30 and 300 K. The conversion rates and $CH_3OH$ yields under the 30 K beam are very similar to those under the 300 K beam at all ice temperatures, demonstrating that the reaction is independent of beam temperature. The dependence of the conversion rates on ice temperature is consistent with that for previous experiments on CO hydrogenation. The conversion rate for $H_2CO \rightarrow CH_3OH$ at 15 K was found to be about half that for $CO \rightarrow H_2CO$. The dependence of the reactions on the initial thickness of $H_2CO$ was also measured. More than 80% of $H_2CO$ was converted to $CH_3OH$ for $H_2CO$ layers of less than 1 monolayer in average thickness. Irradiation of $CH_3OH$ with H atoms did not produce $H_2CO$, demonstrating that the reverse process, $CH_3OH \rightarrow H_2CO$ (H abstraction), is minor compared to the forward process.

*Subject headings:* astrochemistry — dust, extinction — ISM: molecules — molecular processes
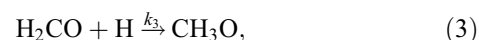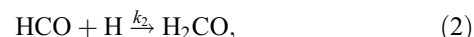
## 1. INTRODUCTION

Surface hydrogenation reactions at low temperatures play an important role in the evolution of molecules on interstellar ice, as well as in energetic processes such as photolysis of ice. In particular, in the core of dense molecular clouds, reactions involving hydrogen atoms could become important compared to photolysis because of the weak photon field. To date, many models involving surface reactions have been proposed, constructed mainly on the assumption that the surface reactions proceed immediately with a probability of unity in the absence of relevant experimental data. Therefore, it is highly desirable to obtain more detailed information on elementary surface reactions, such as activation energies and reaction rates, in order to understand and construct an accurate chemical-reaction network that includes surface reactions.

Among the various hydrogenation reactions, the hydrogenation of CO on the surface of dust has fascinated many theorists because CO is an abundant and primordial molecule in molecular clouds. Theoretical models (e.g., Tielens & Whittet 1997) have suggested that the successive hydrogenation of CO is a key process in the production of simple organic molecules such as $CH_3OH$, which is observed abundantly not only toward high-mass protostars (Dartois et al. 1999) and comets (e.g., Crovisier & Bockelée-Morvan 1999) but also toward low-mass protostars (Pontopiddan et al. 2003). Recent experimental studies by our group have revealed that the formation of methanol proceeds more efficiently by the hydrogenation of CO via $H_2CO$ than photolysis (Schutte et al. 1996) or proton bombardment (Hudson & Moore 1999) under conditions found in molecular clouds (Watanabe & Kouchi 2002; Watanabe et al. 2003, hereafter WSK03). In these studies, significant $H_2CO$ and $CH_3OH$ production from an $H_2O$-CO mixed ice was observed under irradiation with an atomic hydrogen beam below 20 K. On the other hand, the formation of methanol was not observed and the yield of $H_2CO$ was very poor in the experiments on hydrogenation of CO using pure solid CO by another group (Hiraoka et al. 2002). Woon

(2002) attempted to explain these results by calculation of the activation energies. He concluded that the hydrogenation of CO would not be efficient unless tunneling through the activation barrier of about 5–6 kcal molecule$^{-1}$ is efficient. He also reported that water ice is not a good catalytic substrate for $H + CO$ and $H + H_2CO$. However, he has not taken into account the sticking probabilities of H on either $H_2O$ or CO.

We believe that the difference between our results and those of Hiraoka's group arises mainly from the low flux of hydrogen atoms in their experiments and the use of a pure CO target. The hydrogenation of CO in pure solid CO is considered to be relatively suppressed in comparison with that in CO-$H_2O$ mixed ice (Watanabe et al. 2004). The comparison of our previous results with those of the other group are made in § 3.

The pathway for the evolution of CO to $CH_3OH$ by hydrogenation would be $CO \rightarrow HCO \rightarrow H_2CO \rightarrow CH_3O \rightarrow CH_3OH$ (Woon 2002). The intermediate $CH_3O$ may be replaced with $CH_2OH$. From the reported binding energies of these molecules (Bruna et al. 1997; Bauschlicher et al. 1992), until the third step in which $CH_3O$ is formed, reactions with $H_2$ molecules, i.e., $CO + H_2 \rightarrow HCO + H$, $HCO + H_2 \rightarrow H_2CO + H$, and $H_2CO + H_2 \rightarrow CH_3O + H$, are clearly endothermic. In fact, the $CO + H_2 \rightarrow H_2CO$ reaction was not observed in our previous study (WSK03). For the final step, although the reaction $CH_3O(CH_2OH) + H_2 \rightarrow CH_3OH + H$ is slightly exothermic, the exothermicity is much lower than that for the H-addition reaction $CH_3O + H \rightarrow CH_3OH$. Therefore, CO must evolve via the successive addition of H atoms to $CH_3OH$, leading to the following putative reactions (WSK03):

$$CO + H \xrightarrow{k_1} HCO, \qquad (1)$$

$$HCO + H \xrightarrow{k_2} H_2CO, \qquad (2)$$

$$H_2CO + H \xrightarrow{k_3} CH_3O, \qquad (3)$$
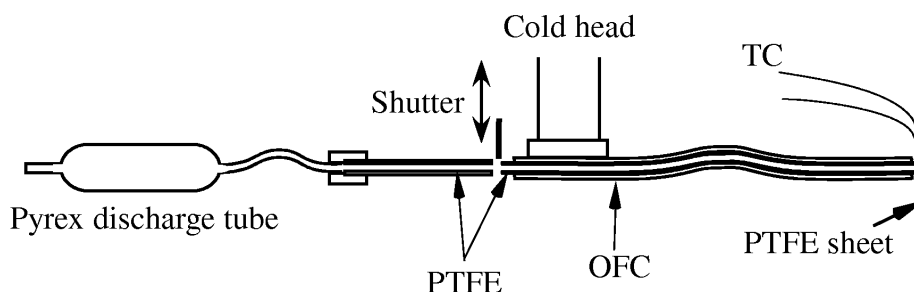
$$CH_3O + H \xrightarrow{k_4} CH_3OH, \qquad (4)$$

Fɪɢ. 1.—Diagram of atomic hydrogen transport line. OFC: Oxygen-free copper tube. TC: AuFe-chromel thermocouple.

where $k_n$ is a rate constant. For these reactions, $k_1 \ll k_2$ and $k_3 \ll k_4$; the reverse processes (H abstraction by H atoms) of reactions (1) and (2) are minor.

Unfortunately, since a series of four individual H-atom additions were measured simultaneously in the previous study (WSK03), a large number of parameter fittings are necessary to obtain the rates for individual reactions (1)–(4) from the data. Of course, the rate for reaction (1) can be readily obtained by a single exponential fitting to CO depletion. However, calculating the rate constant for reaction (3) requires fitting at least four rate equations. To estimate the reaction rate for H$_2$CO → CH$_3$OH, driven by $k_3$, and for the reverse process more directly without the ambiguity of many parameter fittings, a further experiment was performed in the present study examining specifically the hydrogenation of H$_2$CO on H$_2$O ice.

## 2. EXPERIMENTAL

The apparatus, the LAboratory Setup for Surface reactions in Interstellar Environments (LASSIE), used for the present experiment is almost the same as that described previously (Watanabe & Kouchi 2002; WSK03), except for one modification of the transport line for atomic hydrogen. Figure 1 shows a diagram for the atomic-hydrogen transport line. An oxygen-free copper pipe (37 cm) is brought into tight contact with the outside of the polytetrafluoroethylene (PTFE) tube and connected to the cold head of the He refrigerator. The pipe is bent to provide a non–line-of-site geometry, ensuring that the hydrogen atoms collide many times with the PTFE tube. This simple arrangement produces very low temperature atomic hydrogen (Walraven & Silvera 1982; Perry et al. 2002). In the present study, the atomic hydrogen was cooled to 30 K, as measured using an AuFe-chromel thermocouple attached to the PTFE tube at the downstream end.

The experimental procedure is similar to that described previously (Watanabe & Kouchi 2002; WSK03). Briefly, H$_2$O ice was first produced on a cold aluminum substrate by vapor deposition through a capillary plate in an ultrahigh-vacuum chamber (base pressure of ∼10$^{-10}$ torr). The thickness of the H$_2$O ice was about 10 monolayers (ML). H$_2$CO molecules were then deposited at various thicknesses on the ice via another gas line. The pipe (0.25 inches [6.4 mm] in diameter) for H$_2$CO deposition was located about 5 cm from the substrate. From the difference of pressure in the chamber with and without the operation of the cold head during admission of H$_2$CO, it was found that more than 90% of H$_2$CO from the pipe sticks directly on the substrate at temperatures below 20 K. H$_2$CO gas was produced by the thermal cracking of paraformaldehyde, by which paraformaldehyde powder (purity 99.8%; Merck) was heated to 57°C in a glass vacuum tube. It

was necessary to maintain the gas line and the variable leak valve at around 60°C in order to prevent condensation of the H$_2$CO inside the gas line. The infrared (IR) absorption spectra of the sample were measured by Fourier transform infrared spectrometry (FTIR) before and during irradiation with atomic hydrogen. The sensitivity of the FTIR measurements depends on the absorption coefficients of the molecules. For CH$_3$OH, the minimum detectable column density is about 10$^{13}$ cm$^{-2}$. A typical IR absorption spectrum for the initial ice sample is shown in Figure 2. All measurements were repeated several times on different days. The reproducibility of the data was very good, indicating that the flux of H atoms was almost invariant. Although the hydrogen atom flux was not measured, it is thought to have been about ∼10$^{15}$ cm$^{-2}$ s$^{-1}$ based on previous estimations (Watanabe & Kouchi 2002). As discussed in WSK03, it is thought that only about 0.1% of all irradiated H atoms are consumed in reacting with H$_2$CO and that most of the H atoms form H$_2$ by recombination. The dissociation fraction was about 15% at least, as shown in Figure 3.

We carefully eliminated undesired experimental factors. A deflector with 100 V cm$^{-1}$ was mounted at the end of the transfer tube of H atoms to remove charged particles and metastable H atoms possibly created in the H source. Photons from the source plasma are blocked at the wall of the bent transfer tube. In fact, no photons were detected when a photodiode was inserted in front of the substrate. We checked the possibility that the H$_2$CO and CH$_3$OH are created in the
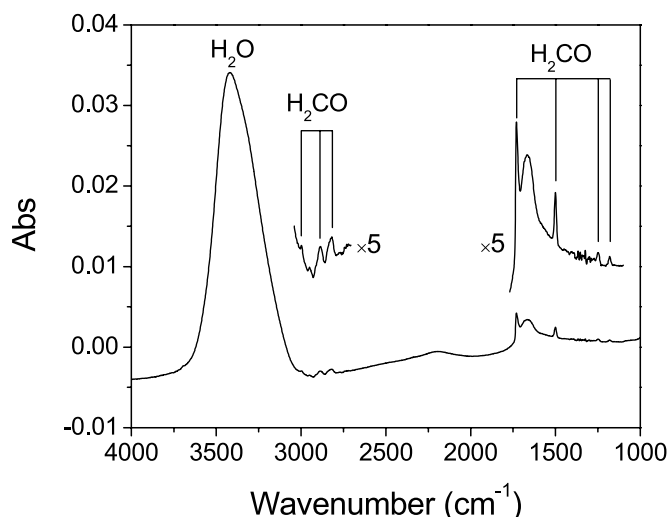


Fɪɢ. 2.—IR absorption spectrum of initial (nonirradiated) H$_2$CO layer of 1 ML average thickness on H$_2$O ice at 15 K.
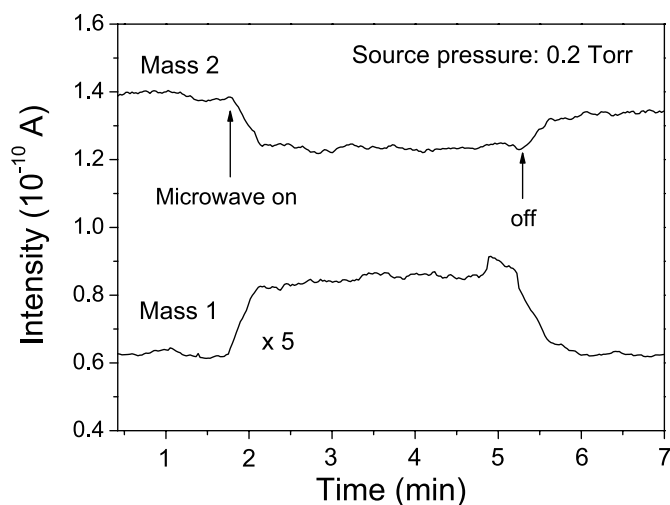
Fig. 3.—Readings from quadrupole mass spectroscopy with the Faraday cup for $H_2$ molecules and H atoms. The intensity of H atoms (mass 1) is magnified by a factor of 5. The microwave for the atomic source was turned on at the time indicated by the arrow.

source but not by the surface reaction. To prevent CO molecules from drifting into the H source, the shutter at the middle of the transfer tube was closed when $H_2O$ and CO gas were deposited on the substrate. Subsequently, a simple test was performed: $H_2O$-CO ice was heated out once, and only $H_2O$ ice was produced. No product was obtained on pure $H_2O$ ice when H atoms were irradiated. If $H_2CO$ and/or $CH_3OH$ are created in the source, these must be obtained even in the pure $H_2O$ case. Furthermore, the dependence of yields on the surface temperature observed in WSK03 is clear evidence that the $H_2CO$ and $CH_3OH$ are created by the surface reaction. If these molecules are created in the source, such temperature dependence should not be observed because the ice temperature ($<20$ K) is far below the evaporation temperatures ($>100$ K) for $H_2CO$ and $CH_3OH$.

## 3. COMPARISON OF OUR PREVIOUS RESULTS WITH THOSE OF ANOTHER GROUP

Before showing the present results, we here compare our previous results on CO hydrogenation (Watanabe & Kouchi 2002; WSK03) with those of Hiraoka's group. Hiraoka et al. (2002) studied the same reaction system and concluded that

the hydrogenation of CO to produce $H_2CO$ and $CH_3OH$ is inefficient under the typical conditions prevalent in molecular clouds. Their conclusion contradicts our previous results. Therefore, it might be desirable to see what the source of these discrepancies might be. We believe that this discrepancy arises mainly from the difference in H-atom flux. In Table 1 we report on a comparison of the experimental conditions and setup used in our and in Hiraoka's experiments. In order to relate the efficiencies of reactions studied in the laboratory to the ones actually present in molecular clouds, the flux of H atoms in laboratory experiments has to be determined. We measured the flux and the dissociation fraction (Watanabe & Kouchi 2002), while Hiraoka et al. did not obtain their estimates experimentally but deduced them from values found in the literature. However, we can obtain information on their H flux from the comparison of the $H_2CO$ yields. In Figure 4 our data (WSK03) on the $H_2CO$ yield with an H irradiation of 30 s are multiplied by 0.027 and plotted against the results of Hiraoka et al. (2002). Our results are very consistent with their results. Taking into account their irradiation time of 60 minutes, their H flux must be about 3 orders of magnitude smaller than our H flux. Furthermore, it should be noted that the $CH_3OH$ yields are considerably smaller (see Fig. 2 of WSK03) even in our measurements at 30 s of irradiation. Therefore, it is reasonable that they did not observe $CH_3OH$ yields in their experiments. The H dose in their experiment of over 60 minutes is about $10^{16}$ cm$^{-2}$ even though their flux is $10^{13}$ cm$^{-2}$ s$^{-1}$ as they claimed. This dose is less than that which occurs over $10^4$ yr in the core of dense molecular clouds, assuming that the number density of H is 10 cm$^{-3}$ and that the temperature is 10 K.

In general, the irradiation times in beam experiments should be carefully set because the background residual gas can cover the sample surface during irradiation. For example, when leaving the sample in a background pressure of $10^{-10}$ torr for about 2 hr, 1 ML of residual gas will be deposited on the surface. This coverage can affect the reactivity of CO on the surface. Since the chamber pressure during H irradiation is normally much higher than $10^{-10}$ torr, the coverage effect from undesired residual gases such as $H_2O$ becomes more significant. Therefore, very long irradiation should be avoided. In the present experiment, we checked the increase in absorbance of $H_2O$ ice during irradiation and found that coverage by the residual $H_2O$ is well below 1 ML after 80 minutes of irradiation. Although both a partial pressure of residual $H_2O$ and the

TABLE 1
Comparison of Experimental Conditions with Those of the Other Group

| Condition | Present Work | Hiraoka et al. (2002) |
|---|---|---|
| Pressure in sample area during the H irradiation (torr)................................................. | $10^{-7}$ | Not reported |
| Type of H source........................................................................................................ | Microwave discharge | DC discharge |
| Power (W)................................................................................................................... | 100 | Not reported |
| Dissociation fraction ................................................................................................. | >15% | Not measured |
| H flux (cm$^{-2}$ s$^{-1}$)................................................................................................... | $10^{14} \sim 10^{15}$ | $<10^{13}$ (deduced from literature) |
| Elimination of photons, charged particles, and metastable H from the source ............. | OK | OK |
| Temperature of H atoms (K)........................................................................................ | 30, 80, room temperature[a] | $\sim$30 |
| Dose of H atoms (cm$^{-2}$) .......................................................................................... | $10^{17} \sim 10^{18}$ [b] | $<10^{16}$ [c] |
| Corresponding duration in molecular cloud (yr) ........................................................ | $10^5 \sim 10^6$ | $<10^4$ |
| Detection method........................................................................................................ | FTIR and thermal desorption[d] | Thermal desorption |

[a] 80 and 300 K used in Watanabe & Kouchi (2002).
[b] Experimental duration of 80 minutes.
[c] Experimental duration of 60 minutes.
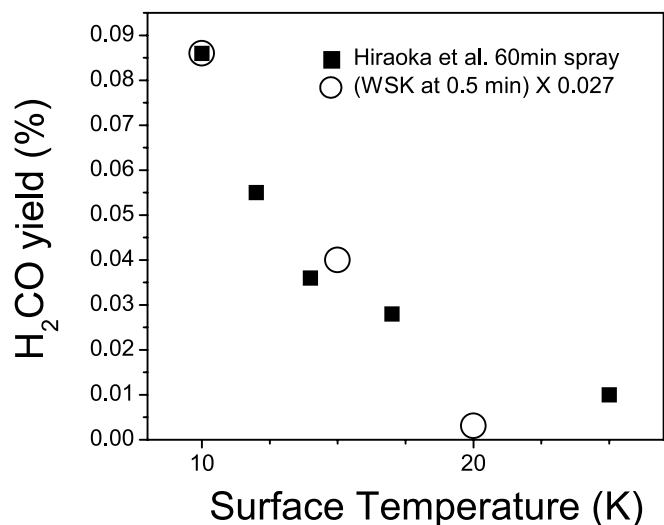[d] Thermal desorption adopted in Watanabe & Kouchi (2002).

therefore that the temperature dependence of the yields is somewhat different from that for $H_2O$-CO ice (Watanabe et al. 2004). However, the obtained yields were fairly consistent with those of the hydrogenation of CO on $H_2O$-CO mixed ice. Here we just show the variation of IR absorption spectra for pure CO ice with irradiation of H atoms in Figure 5. One can see clearly the formation of $H_2CO$ and $CH_3OH$. We conclude that the poor yield of $H_2CO$ and the lack of any $CH_3OH$ yield in Hiraoka's experiments arise from the low flux of H atoms, and we believe that their conclusion that the hydrogenation of CO to produce $H_2CO$ and $CH_3OH$ is inefficient under the conditions of molecular clouds is not very convincing.

The H fluxes of both our and Hiraoka's experiments are much higher than the $10^5$ cm$^{-2}$ s$^{-1}$ expected in the core of clouds. This excessive flux in the experiments is unavoidable when simulating in the laboratory phenomena in space. However, since the individual hydrogenation process proceeds in proportion to the coverage of hydrogen atoms on the surface, the difference with the flux from the space is not essential in evaluating the reaction rates. On the other hand, since the probability of H-H recombination is proportional to the square of the surface coverage, the fraction of H atoms used for recombination in the experiments must be larger than that in molecular clouds, where the H flux is much lower. That is, in molecular clouds the hydrogenation process would be enhanced compared to the recombination process.

## 4. RESULTS AND DISCUSSION

Figure 6 shows the variation in the IR absorption spectra during irradiation with 30 K hydrogen atoms at 15 K. Peaks above and below the baseline indicate an increase and decrease, respectively, in absorbance from the initial (nonirradiated) spectrum (Fig. 2). The initial column density of $H_2CO$ was equivalent to that for 1 ML, assuming an absorption coefficient of $A(H_2CO) = 9.6 \times 10^{-18}$ cm molecule$^{-1}$ (Schutte et al. 1993), which is the C—O stretching mode at 1722 cm$^{-1}$. It should be noted that since the surface of $H_2O$ ice would be



FIG. 4.—$H_2CO$ yields relative to the initial CO. *Filled squares*: $H_2CO$ yields obtained after 60 minute H spray in the experiments of Hiraoka's group (Hiraoka et al. 2002). *Open circles*: $H_2CO$ yields after 30 s of irradiation in our previous experiments (WSK03), multiplied by 0.027.

coverage of $H_2O$ during H irradiation were not reported in Hiraoka et al. (2002), it is desirable information for evaluating the coverage effect.

One might consider that the difference in the ice composition might be the cause of the difference in the results. We also performed experiments with pure CO ice and found that the reactions are suppressed at temperatures above 15 K and
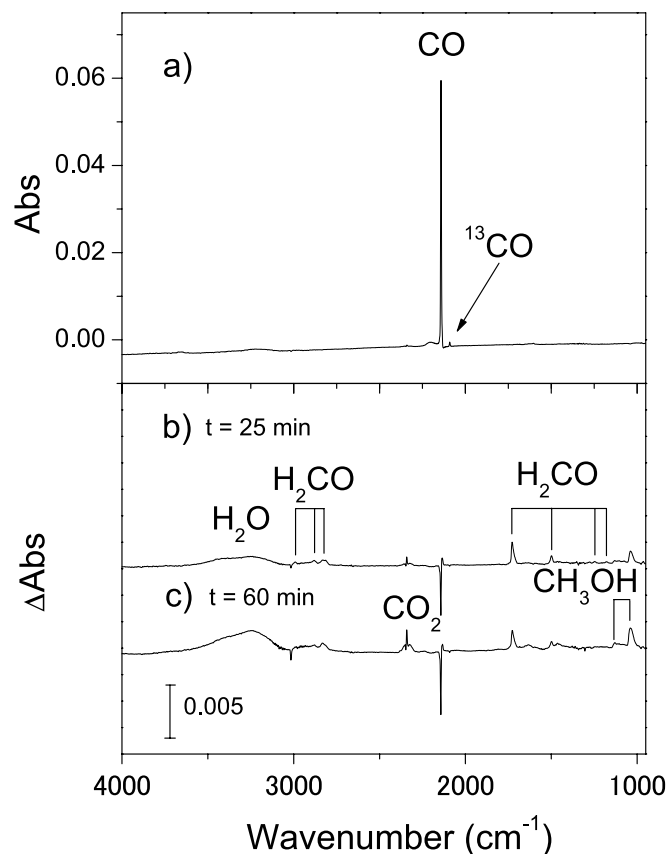


FIG. 5.—(*a*) Initial IR absorption spectrum for pure CO. (*b*) Variation of the IR absorption spectrum after 60 minutes of irradiation of H atoms at 15 K. The slight increase in $H_2O$ ice is due to sticking of the background.
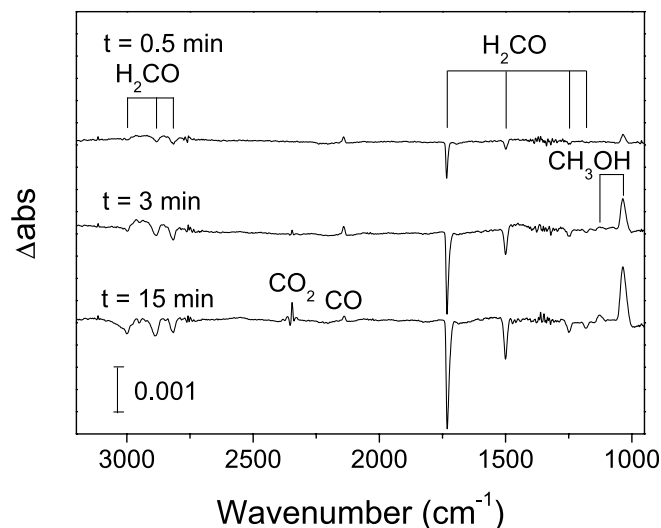


FIG. 6.—Spectral variations of $H_2CO$ on $H_2O$ ice after 30 K H-irradiation at 15 K for 0.5 (*top*), 3 (*middle*), and 15 minutes (*bottom*). The initial column density of $H_2CO$ was equivalent to that for 1 ML assuming an absorption coefficient of $A(H_2CO) = 9.6 \times 10^{-18}$ cm molecule$^{-1}$ (Schutte et al. 1993), which is the C—O stretching mode at 1722 cm$^{-1}$. Spectra were obtained by subtracting the initial absorption spectra from the H-irradiated spectra. Peaks below and above the baseline represent decreases and increases in absorbance, respectively.

very rough, the concept of a monolayer of $H_2CO$ from now on differs from the usual idea of a closely packed layer. That is, some of the $H_2O$ molecules will be exposed on the surface even above 1 ML of $H_2CO$, and a fraction of the $H_2CO$ would be aggregated to form partial thin layers of $H_2CO$ even after a deposition of less than 1 ML. It can be clearly seen in Figure 6 that $CH_3OH$ molecules have formed and grown, as indicated by the emergence of peaks at 1032 and 1118 $cm^{-1}$ and a weakening of the $H_2CO$ peaks at 1722, 1499, 1249, 1178, 2991, 2887, and 2832 $cm^{-1}$. No peaks were observed around the wavenumbers reported for the peaks of $CH_3O$ on the surface (Sim et al. 1995) and $CH_2OH$ in the Ar matrix (Jacox 1981). Although the absorption coefficients of solid $CH_3O$ and $CH_2OH$ are unknown, we expect that the absorption coefficients are not far from that of $CH_3OH$ because those species have $C-O$ and/or $O-H$ bonds. Therefore, we conclude that $CH_3O$ and $CH_2OH$ are hardly present and that the signal of these species is under the detection limits. Since the evaporation temperature of $H_2CO$ is about 100 K, $H_2CO$ may be accumulated on the copper shroud of liquid nitrogen temperature during the experiments. The sticking of $H_2CO$ onto the wall of the chamber at room temperature is negligible. We have checked whether the $CH_3OH$ is produced by $H_2CO$ sticking on the copper shroud and subsequently strays into the ice during the measurements: after performing several sets of experiments, pure $H_2O$ ice was produced and exposed to H atoms for 80 minutes (blank test). It was found that the amount of $CH_3OH$ obtained in this blank test corresponds to only a few percent at most. The formation of $CH_3OH$ was not observed when the $H_2CO$ was irradiated with $H_2$, indicating that the $H_2CO + H_2 \rightarrow CH_3OH$ reaction does not proceed under these conditions. A small amount of $CO_2$ was observed at all temperatures of ice and beam; it is thought to have derived from residual gas desorbed from the surface of the liquid nitrogen shroud surrounding the sample area upon hydrogen-atom bombardment, as discussed previously (WSK03). The trace amount of CO (2142 $cm^{-1}$) suggests that the reverse processes of reactions (1) and (2), H abstraction by H, proceeds to a limited extent. The $H_2O$ peak decreases by $\sim$2% of the initial amount, perhaps mainly because of H and/or $H_2$ impact, because the amount of $H_2O$ loss was almost the same percentage when only $H_2$ molecules were irradiated to produce pure $H_2O$ ice.

The most favorable path for $CH_3OH$ formation is expected to be via reactions (3) and (4) (Woon 2002). An alternative reaction,

$$CH_3O + H_2CO \rightarrow CH_3OH + HCO, \qquad (5)$$

is also a possible channel in the thermal gas phase (Henon & Bohr 2001). However, reaction (5) is unlikely to occur at the present ice temperatures because heavy molecules such as $H_2CO$ cannot readily migrate. Woon (2002) also proposed the formation of $CH_4$ by the following reactions:

$$CH_3O + H \rightarrow OH + CH_3, \qquad (6)$$

$$CH_3 + OH + 2H \rightarrow H_2O + CH_4. \qquad (7)$$
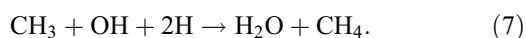
Since the absorption coefficient of $CH_4$ ($\sim$1302 $cm^{-1}$) is comparable to those of $H_2CO$ and $CH_3OH$ (Hudson & Moore 1999), $CH_4$ would be detectable if present. However, the formation of $CH_4$ was not observed in the present experiments

and therefore must represent only a very minor process at best.

Figure 7 plots the variations in column densities of $H_2CO$ (1722 $cm^{-1}$) and $CH_3OH$ (1032 $cm^{-1}$) for 300 K and 30 K H-beams at ice temperatures of 10, 15, and 20 K. The column densities were calculated from the integrated absorbances and absorption coefficients of $9.6 \times 10^{-18}$ and $1.6 \times 10^{-17}$ cm molecule$^{-1}$ for $H_2CO$ (Schutte et al. 1993) and $CH_3OH$ (Kerkhof et al. 1999), respectively. The column densities are normalized to that of initial $H_2CO$. The column density for $H_2CO$ consumption is not always equal to that for the $CH_3OH$ yield. If all of the $H_2CO$ molecules on the surface are immediately converted to $CH_3OH$, the column densities should be the same. This discrepancy in the variation of column densities is discussed below. Here our discussion concentrates on the dependence on ice and beam temperature.

For the 300 K beam, the conversion rate, obtained from the gradient of plots in the earliest period of irradiation, and the $CH_3OH$ yield are highest at 15 K. At 20 K, the conversion rate is lowest but the $CH_3OH$ yield eventually exceeds that at 10 K. However, the difference in the rate between 10 and 20 K is much smaller than that for $H_2CO$ production from CO (WSK03). Considering that the observed conversion rates are determined by reaction-rate constants and sticking probabilities, the features observed above can be explained qualitatively as follows. The fall of the conversion rate at 20 K may be due, not to a lower reaction-rate constant, but to reduction in the sticking probability of H at 20 K, as described previously (WSK03). For the conversion of CO to $H_2CO$, the reaction-rate constant at 10 K would be similar to that at 20 K because the reaction proceeds by the tunneling effect, which is characterized as having a temperature-independent rate constant. In contrast, for $H_2CO \rightarrow CH_3OH$, the dependence of the rate constant on the ice temperature may lie in a transitional stage between the Arrhenius dependence and the low-temperature plateau of the tunneling reaction. The rate constant at 20 K must therefore be larger than that at 10 K, partially compensating for the lower sticking probability. The higher yield of $CH_3OH$ at 15 K compared to 10 K suggests that the diffusion length of H atoms on ice becomes longer as the temperature increases, promoting reaction with larger amounts of $H_2CO$. In fact, the yields at 20 K would eventually become highest if the data were extrapolated to longer irradiation times. Compared to the results in the previous study (WSK03), the $CH_3OH$ yield at 20 K is substantially higher because the parent molecule of $H_2CO$ was present as an initial component in the present experiments, whereas in the previous experiments $H_2CO$ was produced slowly from CO. This difference in the initial conditions significantly affects the final yield of $CH_3OH$.

For the 30 K beam, the ice-temperature dependencies are very similar to those for the 300 K beam, and the conversion rates and $CH_3OH$ yields are also consistent with those for the 300 K beam. Thus, the surface hydrogenation of $H_2CO$ is considered to proceed almost independently of the temperature of the incident H atoms, meaning that H atoms react after thermalization at the ice temperature and not during the loss of the initial kinetic energy.

As shown in Figure 7, $H_2CO$ depletion and $CH_3OH$ formation become saturated at long irradiation times. These saturation values of column density at 15 K are plotted as a function of initial thickness of $H_2CO$ in Figure 8. The yields of $CH_3OH$ increase with the initial thickness up to about 1–1.8 ML, becoming almost constant for thicker layers. This
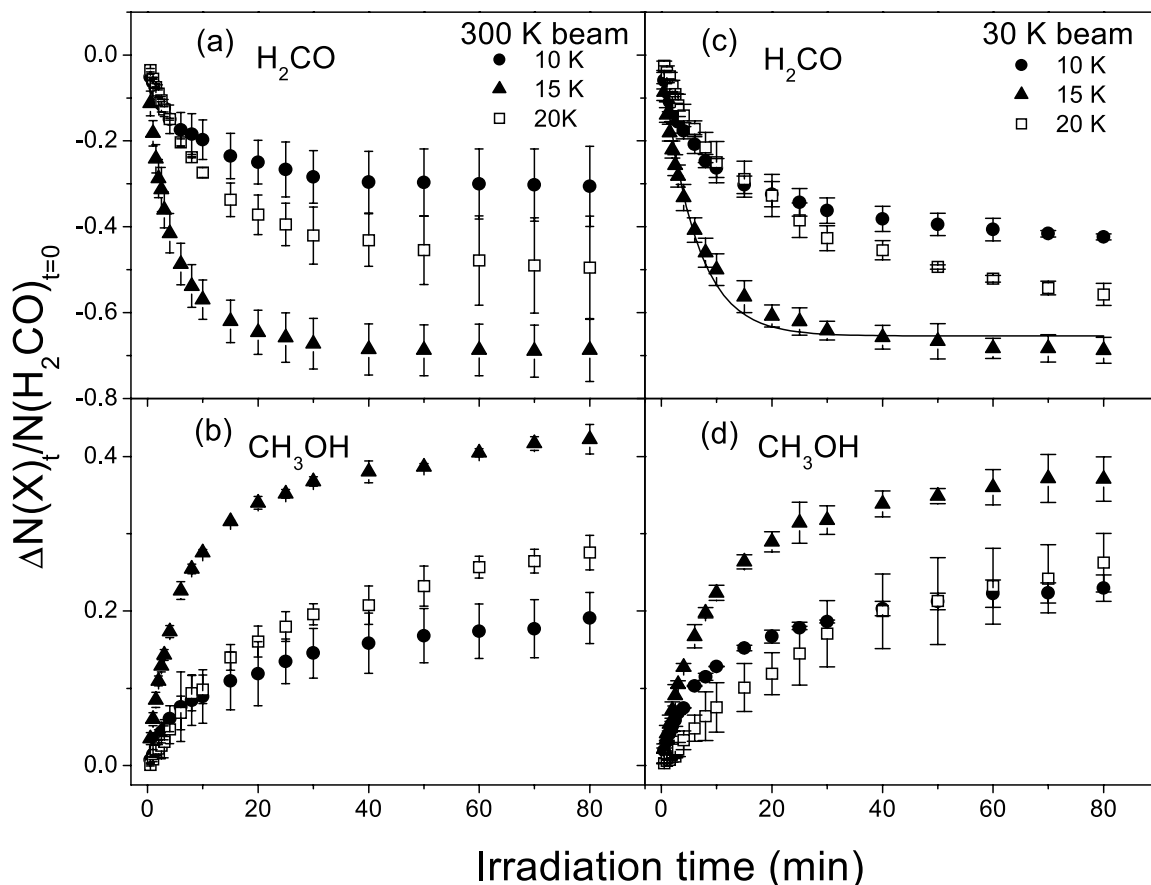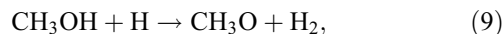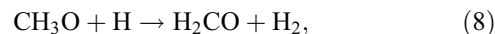
Fig. 7.—Variations in column densities for 1 ML H$_2$CO sample as a function of H-irradiation time at 15 K for (a) H$_2$CO and (b) CH$_3$OH using a 300 K H-beam, and for (c) H$_2$CO and (d) CH$_3$OH using a 30 K H-beam. The solid line in (c) is a fitting curve given by eq. (10). The error bars represent statistical errors.

feature implies that the hydrogenation reaction occurs only around the surface of H$_2$CO on H$_2$O ice at 15 K, while buried H$_2$CO remains intact probably because of obstruction of H atoms by surrounding H$_2$CO molecules. The saturation values of H$_2$CO depletion relative to the initial amount of



Fig. 8.—Column densities of H$_2$CO decrease and CH$_3$OH increase after 30 K H-irradiation for 80 minutes at 15 K as a function of initial thickness of H$_2$CO. Numbers in parentheses represent the fraction of H$_2$CO decrease relative to initial H$_2$CO as a percentage.

H$_2$CO are shown as percentage terms in parentheses in Figure 8. At about 0.4 ML, more than 80% of initial H$_2$CO is eventually consumed, leaving less than 20% of the initial H$_2$CO unreacted. Extrapolation of the data also suggests that more H$_2$CO will be consumed at thicknesses less than 0.4 ML. In chemical equilibrium, the ratio of the rate constant of the forward reaction $k_f$ to that of the reverse reaction $k_r$ is equivalent to the ratio of the product density to the remaining reactant density, that is, $k_f/k_r = $ CH$_3$OH/H$_2$CO in the present case. Therefore, the present result for $\sim$0.4 ML indicates that reverse processes (reformation of H$_2$CO by H-abstract reactions),

$$\text{CH}_3\text{O} + \text{H} \rightarrow \text{H}_2\text{CO} + \text{H}_2, \qquad (8)$$

$$\text{CH}_3\text{OH} + \text{H} \rightarrow \text{CH}_3\text{O} + \text{H}_2, \qquad (9)$$

are very minor. To obtain direct evidence for this, CH$_3$OH on H$_2$O ice was irradiated with H atoms at 10–20 K. Even after 2 hr of irradiation, no products were observed. The present results have shown that balance with the reverse process is unlikely. Although the origin of the difference in the convergence ratio of CH$_3$OH to H$_2$CO between the present and previous results (WSK03) is not clear, it may be that in the previous study, the codeposition of parent CO molecules with H$_2$O may have resulted in the burial of a significant fraction of CO. Thus, the channels to the buried CO from the ice surface would have been very narrow and the
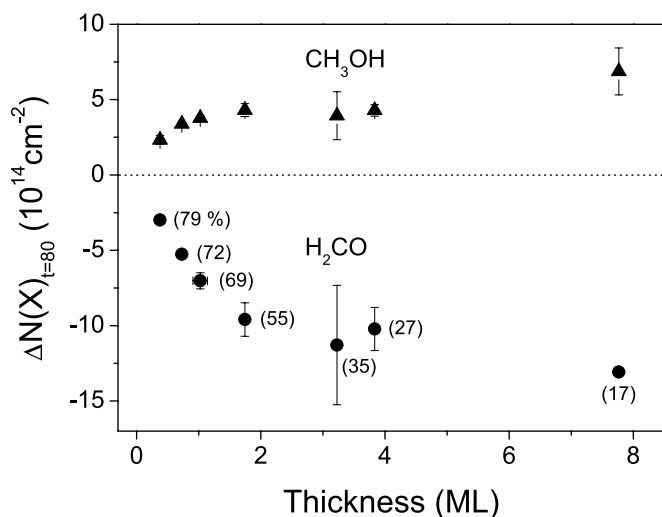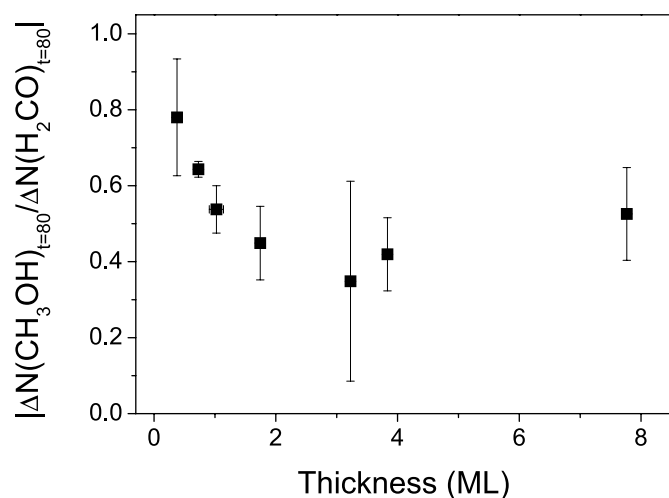
number of H atoms reaching the buried CO would have been limited because of the low diffusion rate. The channels might even have been constricted or closed because of deformation of the ice structure by reaction heat during $H_2CO$ production. The ratio of $CH_3OH$ to $H_2CO$ for 15 K ice clearly increased with the decrease of layer thickness in the previous study. Based on the present argument, this would be attributable to a decrease in the number of buried CO with decreasing thickness. That is, for thinner layers, most of the CO would be exposed on the surface and therefore would eventually turn to $CH_3OH$. The conditions of the present experiment for $\sim 1$ ML of $H_2CO$ are considered to be similar to this situation.

Figure 9 shows the ratio of estimated column densities between $H_2CO$ depletion and $CH_3OH$ yield against the initial thickness of $H_2CO$. As described above, if all of the observed decrease in $H_2CO$ is converted immediately to $CH_3OH$ without desorption, the ratio should be about unity, independent of the initial thickness of $H_2CO$. However, as shown in Figure 9, the ratio is less than unity and varies from 0.8 to 0.4 as the $H_2CO$ thickness increases. Although the estimation of absorption coefficients in the literature must have some errors that lead to the inconsistencies in the calculated column densities in the present results, the systematic variation of the ratio cannot be explained by the errors. Furthermore, the ratio tends to converge to unity as the $H_2CO$ thickness decreases. This implies that at least the relative values of absorption coefficients for $H_2CO$ and $CH_3OH$ in the literature are approximately correct.

There are two possible explanations for this variation. The first is that the absorption coefficients vary with the initial thickness of $H_2CO$. If unique values of absorption coefficients are used for estimation of the column densities, a discrepancy arises between the estimated and actual column densities. Below 1 ML, $H_2O$ and $CH_3OH$ molecules coexist with $H_2CO$ on the surface, whereas for thicker layers, the components of the surface are mainly $H_2CO$ and $CH_3OH$. In the case of very thin ice, the $H_2O$ component on the surface becomes important and the interaction of $H_2CO$ with $H_2O$ is enhanced, possibly resulting in a slight change in absorption coefficients. Schutte et al. (1993) and Kerkhof et al. (1999) studied the influence of $H_2O$ on the absorption coefficients for $H_2CO$ and $CH_3OH$, respectively. For $H_2CO$, the absorption coefficient changes

little when the ratio of $H_2O$ to $H_2CO$ varies from 0 to 33. For $CH_3OH$, the absorption coefficients decreases slightly with increasing $H_2O$ fraction, from $1.9 \times 10^{-17}$ cm molecule$^{-1}$ at an $H_2O/CH_3OH$ ratio of 1 to $1.4 \times 10^{-17}$ cm molecule$^{-1}$ at a ratio of 40. Therefore, even though the actual column density does not change, the estimated column densities of $CH_3OH$ can change by up to 20% when a single value of $1.6 \times 10^{-17}$ cm molecule$^{-1}$ is used for the absorption coefficient, as shown in Figure 9. However, the estimated column densities change by more than 50% and are still well below unity. Therefore, variations in the absorption coefficients due to changes in ice composition are not sufficient to explain the observed variation in the column density ratio.

The second possibility is related to desorption of reacted $H_2CO$ and the surrounding $H_2CO$ during H irradiation. If the $H_2CO$ molecules are consumed not only by conversion to $CH_3OH$ on the surface but also by desorption, the estimated column density of $H_2CO$ depletion will be larger than that for $CH_3OH$. Two desorption processes would proceed in the present system: collision-induced desorption due to incident H and $H_2$, and desorption as a result of reaction heat. To examine desorption by collision of $H_2$ molecules, the $H_2CO$ ice was irradiated with an $H_2$-only molecular beam. The depletion of $H_2CO$ due to $H_2$ impact was only less than 3% of the initial amount of $H_2CO$ for all thicknesses. Although it would be difficult to measure the collision-induced desorption due to H atoms, since the H-atom beam always includes a significant fraction of $H_2$ molecules, the effect must also be minor because the momentum of the H atom is smaller than that of $H_2$ and the heat of physisorption of H atom onto $H_2O$ is similar to that for $H_2$ (Leitch-Devlin & Williams 1984; Buch & Zhang 1991). On the other hand, it is likely that reacted $H_2CO$, such as the $CH_3OH$ product and/or the $H_2CO$ adjacent to the reaction site, may be immediately desorbed by the heat of the reaction. The number of $H_2CO$ molecules desorbing tends to increase with initial $H_2CO$ thickness because of the increased number of $H_2CO$ molecules around the reaction sites. Unfortunately, measurements of desorbed species by quadrupole mass analysis were not successful because of weak signals and poor signal-to-noise ratios. Assuming the absorption coefficients in the literature and the hypothesis of desorption, the ratio of $\sim 0.4$ for the column densities below 1 ML indicates that 60% of reacted $H_2CO$ desorbs immediately because of the heat of the reaction.

Finally, CO hydrogenation on $H_2O$ ice at 15 K was also conducted in order to compare the reaction-rate constants $k_1$ and $k_3$. Although CO hydrogenation was measured in the previous study (WSK03), the initial ice conditions (i.e., parent molecules) were different from those in the present experiment, and the difference in ice structure may influence the reaction rates and saturation. In the present experiment, CO molecules were deposited to a thickness of 1 ML on pure $H_2O$ ice, and the specimen was irradiated with H atoms at 15 K. The variation in column densities for CO and products are plotted in Figure 10. The column densities were calculated by using absorption coefficients from the literature (Gerakines et al. 1995; Schutte et al. 1993; Kerkhof et al. 1999). The loss of CO column density is smaller than the sum of increased $H_2CO$ and $CH_3OH$. This could be due to errors in the estimated absorption coefficients, as mentioned above. More precisely, the estimated absorption coefficient for CO could be relatively larger than those for $H_2CO$ and $CH_3OH$. In any case, we here use only the data from the CO decrease. We evaluate relative values of $k_1$ and $k_3$ from CO the decrease in Figure 10 and
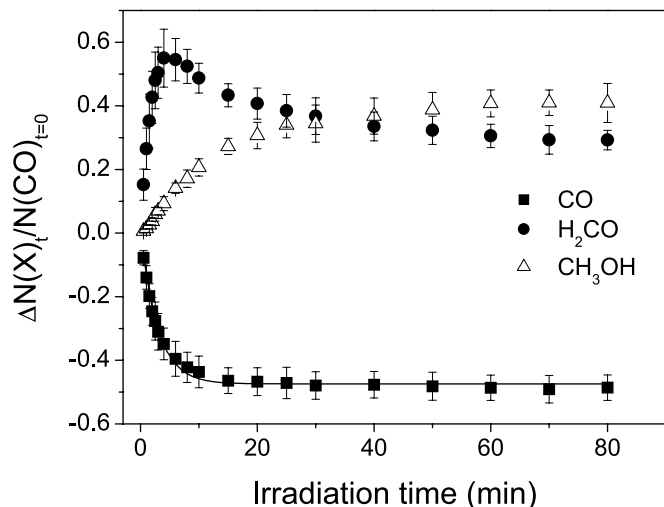
Fig. 10.—Variations in column densities of CO depletion, H₂CO, and CH₃OH after 30 K H-irradiation at 15 K for the CO-on-ice experiment. The solid line is the fitting curve given by eq. (10).

from the H₂CO decrease in Figure 7c, respectively, by the fitting of a single exponential,

$$\frac{\Delta N(X)}{N_0(X)} = \alpha \left(1 - e^{-p[H]k_{1,3}t}\right), \qquad (10)$$

where $N(X)$ is the column density of X, $N_0$ is the initial column density, $\alpha$ is the saturation value, $p$ is sticking probability of H, and [H] is the H-atom flux. We found that the H flux fluctuates little during the experiments. Assuming that the sticking probability is dominated by H₂O and constant, the ratio $k_1/k_3$ was determined to be 2.0. This difference in rate constants is thought to be due to differences in activation energies. In the previous study (WSK03), the value of $k_1$ at 10 K was very similar to that at 15 K, whereas in the present experiment, $k_3$ at 10 K is smaller than that at 15 K. Therefore, the ratio of $k_1/k_3$ is greater than 2.0 at 10 K.

## 5. ASTROPHYSICAL IMPLICATIONS

The present results clearly show that CH₃OH molecules are efficiently produced under the conditions of cold clouds up to around 20 K. Furthermore, the production rates of CH₃OH depend only on the ice temperature, not on the temperature of hydrogen atoms (in the range 30–300 K). When combined with the previous results (WSK03), it is evident that successive hydrogenation of CO on ice represents the main route to H₂CO and CH₃OH. Since the reverse processes by H abstraction from CH₃OH are minor, energetic processes such as UV-photon impact are necessary to decompose CH₃OH. Therefore, in dense clouds where the photon field is very weak, CH₃OH would remain as a terminal molecule, and the abundances of CH₃OH in clouds would be determined by competition between H-atom and photon flux. The results of measurements of the dependence on H₂CO thickness indicate that H atoms can react only with surface H₂CO, not with molecules in the bulk, at least in the present experiments. This implies that the continuous supply of parent H₂CO or CO onto CH₃OH on ice surfaces is the most feasible way to produce the abundant solid CH₃OH observed (e.g., Dartois et al. 1999; Pontopiddan et al. 2003). On the other hand, if significant amounts of solid CO covered the ice surfaces at some time, it would be difficult to convert CO within the solid to CH₃OH.

The obtained ratio of $k_1$ to $k_3$ has important implications for chemical modeling. In the models of surface reactions presented to date, rate constants or reaction probabilities have been determined by activation energies that have been either estimated theoretically or regarded as unknown factors because of lack of experimental data (e.g., Caselli et al. 2002). The present results show that the conversion CO → H₂CO proceeds more readily than H₂CO → CH₃OH.

Finally, the desorption of H₂CO during reaction as suggested here may represent a crucial process that releases adsorbed species into the gas phase. Further experiments will be necessary to confirm this hypothesis.

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