

Formation and Deuterium Fractionation of Organic Molecules on Grain Surfaces

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Abstract. A series of experiments on the surface reactions of hydrogen and deuterium atoms with solid CO, formaldehyde (H_2CO), and methanol (CH_3OH) has been performed. Successive hydrogenation of CO on surfaces at ~ 10 K was found to proceed efficiently via tunneling to produce H_2CO and CH_3OH on dust grains under the typical conditions of molecular clouds. Formation rates are strongly dependent on the surface temperature and composition. The role of surface reactions in the formation of deuterated formaldehyde and methanol was investigated. The deuterium fractionation of methanol observed in molecular clouds was reproduced experimentally via H-D substitution in solid methanol at an accreting atomic D/H ratio of 0.05–0.1. This is the first evidence that grain-surface reactions can be responsible for fractionation. We have determined several effective rate constants for hydrogenation, deuteration, and H-D substitution to construct the surface reaction network for CO, H_2CO , CH_3OH , deuterated formaldehyde, and deuterated methanol.

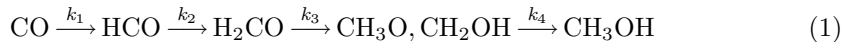
Keywords. astrochemistry — dust, extinction — ISM: molecules — molecular processes

1. Introduction

In observations, large numbers of solid-phase molecules have been discovered on interstellar dust in molecular clouds. Among the observed solid-phase molecules, primordial species such as CO must first be produced in the gas phase and subsequently freeze on a cold dust surface, while it is widely accepted that the formation of the dominant H_2O molecules and more complex species requires surface chemical processes (for a review see Ehrenfreund & Charnley 2000; Boogert & Ehrenfreund 2004). Many experiments have been performed to simulate grain-surface processes and to analyze the observed infrared absorption spectra. These experiments were successful to some extent in revealing the importance of the photolysis and ion-bombardment of ice and in enabling the molecular assignment of the observed spectra. However, quantitative information on surface processes such as reaction channels, reaction rates, and activation energies, has yet to be obtained. In particular, details of nonenergetic processes, namely, surface reactions of light atoms, are as yet not well known despite their importance in the cold quiescent region.

Formaldehyde (H_2CO) and methanol (CH_3OH) have been found abundantly in not only interstellar ice (e.g., Keane *et al.* 2001) and but also in comets (e.g., Crovisier & Bockelée-Morvan 1999). It has been reported that pure gas-phase reactions (e.g., Shalabiea & Greenberg 1994) and UV photolysis of H_2O -CO ice (Allamandola *et al.* 1988; Schutte *et al.* 1996) are insufficient for explaining the observed abundances of these organic molecules in interstellar ice. In proton bombardment experiments, Hudson and Moore (1999) demonstrated that, over 4.6 billion years in space, yields of H_2CO and CH_3OH from H_2O -CO ice would be up to 7% and 12%, respectively. This process is effective for explaining the production of methanol in a comet's nucleus only. Theoretical

models suggest that the successive addition of hydrogen atoms (hydrogenation) to CO:



where k_n is the reaction rate, takes place on the dust surface via tunneling reactions through activation barriers as large as 1000–2000 K and produce H_2CO and CH_3OH even at a temperature of approximately 10 K (Tielens & Allamandola 1987; Tielens & Whittet 1997). These models stimulated experimental works on the hydrogenation of CO. Hiraoka *et al.* (1994; 2004) experimentally investigated this reaction system with an H atom spray apparatus. They observed only a small amount of H_2CO and no CH_3OH products upon exposure of pure solid CO to H atoms and concluded that the hydrogenation of CO would be too slow to produce H_2CO and CH_3OH on a grain surface. Unfortunately, however, they did not experimentally estimate the flux of hydrogen atoms that they used. The estimation of the H flux or fluence is essential to determine the efficiency of reactions in molecular clouds. The comparison of our experimental results described below and theirs enabled us to estimate their flux to have been $10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ or less. This low flux most likely explains their results (Hidaka *et al.* 2004; Watanabe *et al.* 2005).

Recent observations have revealed that the abundances of some deuterated interstellar molecules are markedly larger than the cosmic D/H ratio of 10^{-5} . In particular, deuterium fractionation in methanol was found in not only molecular clouds (Parise *et al.* 2003; 2004) but also in comets (Crovisier *et al.* 2004), and the ratio of deuterated methanol to normal CH_3OH in column density observed toward a low-mass protostar is up to approximately 0.4. Hereafter, the term X- d_n will either denote an isotopomer with a specific number n deuterium atoms (e.g. X- d_2) or, if a general n appears, will refer to all deuterated isotopomers of a molecule. It is difficult to reproduce the observed D-enrichments with pure gas-phase models. Although some gas-grain models have been proposed that achieve the observed level of D-enrichments of interstellar methanol, they are rather ambiguous due to the lack of information about grain-surface reactions such as reaction channels and the rates of hydrogenation and deuteration. It is therefore highly desirable to experimentally clarify the role of grain-surface reactions in D-enrichments.

Here, we present the results of our series of recent experiments regarding hydrogenation and deuteration of solid CO, H_2CO , D_2CO , and CH_3OH .

2. Experimental

Two pieces of apparatus, Laboratory Setup for Surface reactions in Interstellar Environment (LASSIE) and Apparatus for Surface Reaction in Astrophysics (ASURA), were constructed on the basis of the same concept for experiments on the surface reactions of atoms. Both systems are of basically the same design and described elsewhere (Hidaka *et al.* 2004; Watanabe *et al.* 2004, 2005). The experiments were performed with LASSIE or ASURA. The reactions of H and D atoms with solid CO, H_2CO , and D_2CO were measured mainly using LASSIE and those with methanol using ASURA. In addition, we sometimes also measured the same reaction system using both LASSIE and ASURA to crosscheck the validity of the experiments. The composition of the samples investigated were CO- H_2O mixed ice, CO (1 eML) on H_2O ice, pure solid CO, H_2CO (1 eML) on H_2O ice, D_2CO (1 eML) on H_2O ice, and pure solid methanol(- d_n). Here, the term “1 eML” represents the equivalent amount of molecules for one monolayer of a flat surface. Since the surface of amorphous H_2O ice is very rough, 1 eML of molecules cannot cover the entire surface area and some H_2O molecules will be exposed on the surface. That is, 1 eML does not represent a coverage of unity.

Solid samples were produced by vapor deposition on an aluminum substrate cooled by a closed-type He refrigerator. In the present work, the surface temperature was varied from 8 to 20 K. H₂CO and D₂CO gases were produced by the thermal cracking of paraformaldehyde (purity 99.8%, Merck) and paraformaldehyde-*d*₂ (purity 99%, ACROS) powders, respectively. The powders were heated to 57 °C in a glass vacuum tube. It was necessary to maintain the gas line and the variable leak valve at approximately 60 °C in order to prevent condensation of H₂CO inside the gas line. The composition of the solid samples were measured using a Fourier transform infrared spectrometer at resolutions of 0.5 cm⁻¹ for pure solid CO and CO-H₂O mixed ice and 4 cm⁻¹ for H₂CO, CO-H₂O mixed ice, and methanol.

Details of the atomic source have been described elsewhere (Hidaka *et al.* 2004; Watanabe *et al.* 2005). Briefly, H and D atoms were produced by the dissociation of H₂ and D₂ molecules in a microwave-induced plasma in a Pyrex glass tube (25 mm in diameter). Atoms were transferred via a series of two polytetrafluoroethylene (PTFE) tubes to the solid target. The downstream PTFE tube was tightly covered with an oxygen-free copper pipe connected to the cold head. This simple arrangement produces very low temperature atomic hydrogen (Walraven & Silvera 1982). In the present study, the beam line was cooled to 30–50 K, as measured using Au/Fe–0.07% chromel thermocouples attached to the PTFE tube at the most downstream end. We carefully eliminated the contamination in the atomic source.

The measurement of atomic flux is essential for the determination of the reaction rates and the efficiency of reactions in space. In our experiments, the fluxes of atoms were measured using a quadrupole mass spectrometer (QMS) with a Faraday cup, calibrated with an ion gauge. During the flux measurements, the substrate was de-installed and the QMS head was set at the original position of the substrate in alignment with the beam line. The typical dissociation fraction was approximately 15% at least. The H atom fluxes were in the range of $5 \times 10^{14} - 1 \times 10^{15}$ cm⁻² s⁻¹.

3. Results and Discussion

3.1. H + CO-H₂O Mixed Ice and H + CO (1 eML) on H₂O Ice

CO-H₂O mixed ice (CO/H₂O ~ 0.25) was exposed to the cold H beam. Molecules of H₂CO and, subsequently, CH₃OH were significantly produced with consumption of CO below 20 K. The sudden decrease in the reaction rates at 20 K is considered to have arisen from the decrease in sticking coefficient of hydrogen atoms on H₂O ice rather than from the decrease in the reaction rate constant (Watanabe, Shiraki, & Kouchi 2003). This surface-temperature dependence implies that the hydrogen atoms react with CO after adsorption and diffusion on the surface: the so-called Langmuir-Hinshelwood process. The formation of these molecules is not observed when a sample is exposed to just H₂ molecules. We also carefully checked for undesirable experimental factors such as contamination by, for example, carrying out a blank test. No such effects were found (Hidaka *et al.* 2004). Furthermore, since reactions of H₂ with HCO and CH₃O are endothermic, we conclude that H₂CO and CH₃OH are produced by the successive reaction (1). The intermediates, HCO and CH₃O (CH₂OH) radicals, were not observed, indicating the relationships among reaction rates to be $k_1 \ll k_2$ and $k_3 \ll k_4$.

Since the column densities of reacted CO were of the order of $10^{15} - 10^{16}$ cm⁻² over the fluence of 10^{18} atoms cm⁻², only 1% or less of the total number of injected H atoms were used for the hydrogenation. A significant number of H atoms would be consumed by H-H recombination to produce H₂ molecules. When the atomic flux decreases, the relative

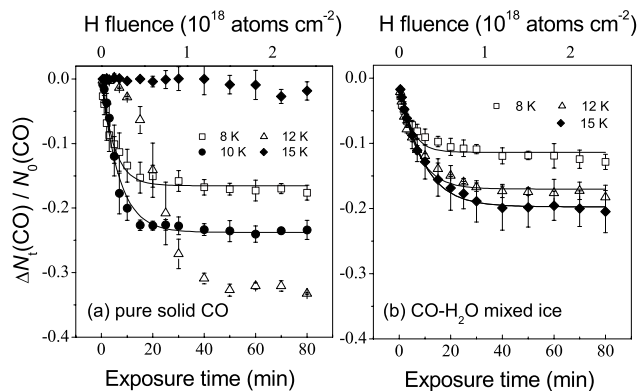


Figure 1. Attenuation of CO-column density upon H exposure for (a) pure solid CO and (b) CO-H₂O mixed ice. The *y*-axis is normalized to the initial column density. Solid lines are least-square fits using eq. (2).

fraction of H atoms used for recombination compared with those used for hydrogenation becomes smaller because the probability of H-H recombination is proportional to the square of the surface coverage. The depletion of CO and the formation of H₂CO and CH₃OH are saturated at long exposure times. It was found that the reason for the saturation is not due to the balance with the reverse process of reaction (1) (H-atom abstraction by another H atom) but the limit of H atom diffusion in bulk (Watanabe *et al.* 2003, 2004). Therefore, the rates of CO decay correspond only to the rates of the first part of reaction (1), namely CO + H → HCO. We also exposed CO (1 eML) on H₂O ice to H atoms. The results were essentially the same as those obtained for mixed ice.

We estimated the reaction rate constants for CO + H → HCO using the fits of CO data (Figure 1) to

$$\frac{\Delta N(\text{CO})}{N_0(\text{CO})} = \alpha (1 - \exp(-kn_{\text{H}}t)) \quad (2)$$

and

$$\frac{dn_{\text{H}}}{dt} = Pf_{\text{H}} - k_{\text{H-H}}n_{\text{H}}^2 - k_{\text{H-CO}}n_{\text{H}}n_{\text{CO}} \quad (3)$$

where α is a saturation value, k the rate constants, P sticking coefficient of atom, f_{H} the flux of H atoms, and n_{H} and n_{CO} the surface densities of H atoms and CO, respectively. In equation (3), we neglect the terms for the reactions of H with HCO, H₂CO, and CH₃O and the desorption of H atoms, because the rates of H-atom loss at the surface by those processes must be very slow. Chigai *et al.* (2005, in preparation) found that, under our experimental conditions, the time variation of n_{H} is governed by the atomic flux (the first term of right side in eq. 3) and the loss due to H-H recombination (the second term) and n_{H} becomes constant immediately. By setting the left side of eq. (3) to zero, we obtained $n_{\text{H}} = 53.9 \times (f_{\text{H}}P)^{1/2} \text{ cm}^{-2}$. Here, the value of $k_{\text{H-H}}$ was estimated by using activation energy of 103 K (Ivliev *et al.* 1982) and a square potential barrier of 1-Å width for the recombination. Consequently, the values of α and the product $k_{\text{H-CO}}P^{1/2}$ (effective rate constants) are determined by the fittings, as shown by the solid lines in Figure 1. The effective rate constants at 15 K are 4.7×10^{-12} and $1.5 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ for H + CO (1 eML) on H₂O and H + CO-H₂O mixed ice, respectively.

3.2. H + Pure Solid CO

Recent investigations of the observed spectra of interstellar ice have revealed the presence of pure solid CO segregated from H₂O ice (Teixeira *et al.* 1998; Pontoppidan *et al.* 2003).

To simulate hydrogenation on such an ice and clarify the role of H₂O ice, 10 ML of pure solid CO was exposed to H atoms. The formation of H₂CO and CH₃OH and nondetection of radicals were observed again. However, as shown in Figure 1, the dependence of the reactions on temperature is stronger than that for CO-H₂O mixed ice. The reactions become very slow at 15 K and the behavior of the CO plot at 12 K is not like a single exponential decay. The smaller sticking coefficient of H atoms on pure solid CO than that on H₂O ice would be responsible for these features. The sticking coefficient on CO may drop at around 12–15 K. The initial stage of the CO-decay curve at 12 K implies that the sticking coefficient gradually increases with exposure time due to the production of H₂CO. The H₂CO produced on CO would enhance the sticking coefficient. In fact, when we deposited 0.3 eML of H₂CO on solid CO in advance and subsequently exposed it to H atoms at 12 K, the shape of the CO decay curve became like that of a single-exponential decay curve similar to that at 10 K (Watanabe *et al.* 2004). We fitted the CO data at 8 and 10 K to eq. (2) and estimated the effective rate constants, which are shown in § 5.

3.3. D + CO (1 eML) on H₂O Ice

In order to compare the deuteration of CO with the hydrogenation of CO, CO (1 eML) on H₂O was exposed to cold deuterium atoms. The flux of deuterium atoms was the same as that of hydrogen atoms for H + CO (1 eML) on H₂O ice. The results will be described in detail elsewhere (Hidaka, Kouchi, & Watanabe 2005, in preparation). Briefly, the products D₂CO and CD₃OD were observed and the temperature dependence of CO decay was similar to that observed for hydrogenation. However, the formation rates of D₂CO and CD₃OD were much slower than those of H₂CO and CH₃OH for hydrogenation. Since the sticking coefficient of D atoms must be very similar to that of H atoms at the same surface temperature, this difference is considered to result from the difference in reaction rate constants. The value of $k_D P^{1/2}$ at 15 K for D + CO → DCO was determined by fitting, using eq. (2). The ratio of deuteration rate constant k_D to hydrogenation rate constant k_H , k_D/k_H , is approximately 0.1 at 15 K. This isotope effect is ascribed to the mass effect of the tunneling reaction.

3.4. H + H₂CO (1 eML) on H₂O Ice

In order to estimate the reaction rates for the hydrogenation of H₂CO directly from the decay of H₂CO, solid H₂CO (1 eML) was produced on H₂O ice and exposed to cold H atoms. CH₃OH was gradually produced with the consumption of H₂CO. We confirmed that H₂CO does not react with H₂. The reaction rate constant k at 15 K relative to that for CO hydrogenation on H₂O ice was obtained by the fitting of H₂CO decay curve to be approximately 0.5 on the assumption that the sticking coefficients are the same because atoms mainly adsorb first on H₂O ice which is a main component at the surface (Hidaka *et al.* 2004).

3.5. H + D (D/H~0.1) + Pure Solid CO (10 ML) and D + Solid CH₃OH (4 ML)

To simulate the formation of deuterated formaldehyde and methanol on grains, pure solid CO was exposed to H and D atoms simultaneously at an atomic flux ratio of D/H~0.1, at which accretion of atoms can be achieved in the gas phase (Roberts *et al.* 2003). Variations in IR spectra observed upon H and D exposure are shown in Figure 2. Peaks corresponding to the products of H₂CO (1729, 1499, 1247, and 1177 cm⁻¹), HDCO (1700 and 1401 cm⁻¹), D₂CO (1684 cm⁻¹), CH₃OH (1039 and 1126 cm⁻¹), CH₂DOH (1330, 1290, and 1047 cm⁻¹), CHD₂OH (1331, 1301, 1091, and 950 cm⁻¹), and CD₃OH (1128 and 982 cm⁻¹) are clearly observed. Radicals and Me-OD (Me; methyl group) were not detected. This seems to be consistent with the low abundance of Me-OD observed in

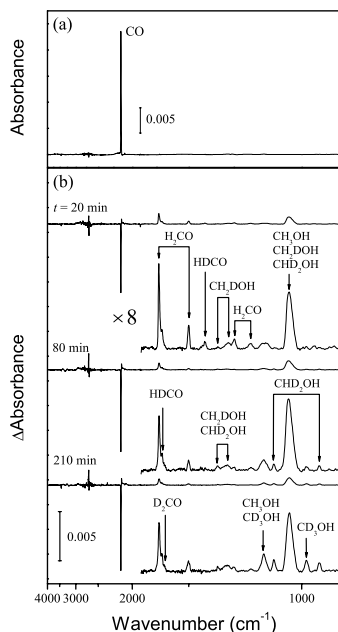


Figure 2. Variation in infrared absorption spectra for simultaneous exposure of solid CO to H and D atoms at 10 K. (a) Initial spectrum prior to exposure. (b) Spectra obtained by subtraction of the initial one from those obtained after the exposure time t .

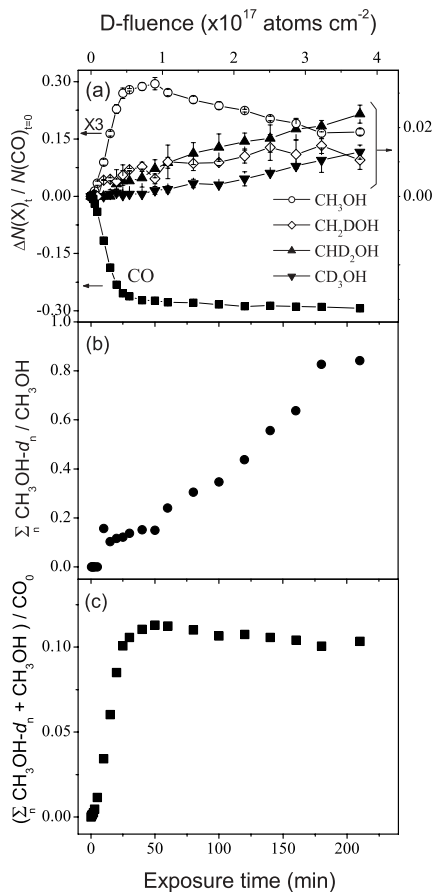


Figure 3. Variation in column densities as a function of exposure time and D fluence. (a) column densities for CO and methanol- d_n . The y-axis is normalized to the initial column density of CO. Note that the left and right y-axes correspond to CO and normal methanol, and methanol- d_n , respectively. (b) Sum of column densities of methanol- d_n relative to column density of CH_3OH . (c) Sum of column densities for methanol- d_n and CH_3OH .

molecular clouds (Parise *et al.* 2004). The variation in column densities for parent CO, CH_3OH , and deuterated methanol and the sum of column densities of methanol- d_n are plotted in

Figure 3(a) and (b), respectively. Figure 3(c) shows a plot of the sum of the column densities for CH_3OH and methanol- d_n normalized to the initial column density of CO. Here, we concentrate on the formation of methanol- d_n and thus do not show the variation in column densities for formaldehyde. From Figure 3(b), one can see that deuterium fractionation progresses with exposure time. By examining Figure 3(a), information on the formation process of methanol- d_n is obtained. The yield of CH_3OH first increased quickly and subsequently reached a maximum. CH_2DOH , CHD_2OH , and CD_3OH were

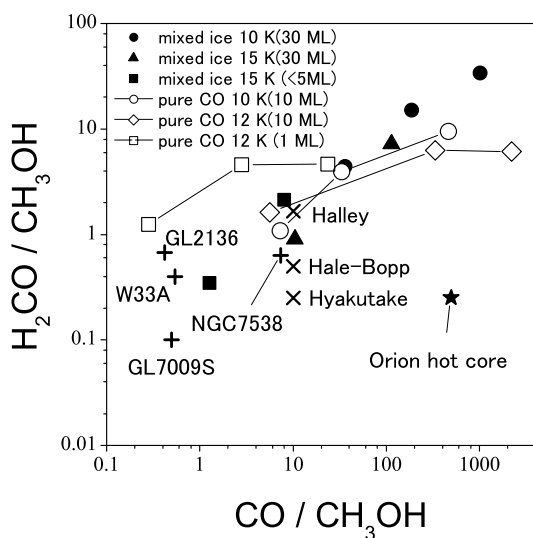


Figure 4. Column density ratios of H_2CO and CO relative to CH_3OH for the experimental and observational results. Open symbols represent results for pure solid CO, solid symbols indicate mixed-ice results, and observations are denoted by + for interstellar ice (Kean *et al.* 2002), x for comets, and \star for the Orion compact ridge (Ehrenfreund & Charnley 2000).

produced in sequence with decreasing amount of CH_3OH . These features cannot be explained by the successive addition of H and D to CO but indicate the occurrence of H-D substitution in methanol after the formation of CH_3OH . In Figure 3(c), the sum of CH_3OH and total deuterated methanol becomes constant after the exposure of 25 min, indicating that H-D substitution in methanol is dominant after that period of time; successive addition and substitution compete until then. As described in the next section, addition of D atoms to formaldehyde ($-d_n$) is very slow. Therefore, substitution would be dominant for the formation of methanol- d_n even before 25 min.

To confirm whether H-D substitution in methanol occurs, solid CH_3OH was exposed to D atoms only. The yields of CH_2DOH , CHD_2OH , and CD_3OH were obtained with the consumption of CH_3OH . The time variation of column densities again clearly reveals successive H-D substitution in methanol (see Fig. 4 in Nagaoka, Watanabe, & Kouchi 2005). When parent solids of CH_3OD , CD_3OH , CHD_2OH , CH_2DOH , and CD_3OD were exposed to H atoms, no reaction was observed. That is, once deuterated methanol (methanol- d_n) is produced, it never returns to its predeuterated state (methanol- d_{n-1}) by reaction with H atoms. Therefore, H-D substitution in methanol on the grain surface can act as the process of deuterium fractionation and thus should be included in the theoretical models. A detailed discussion of this is described elsewhere (Nagaoka *et al.* 2005).

3.6. D + Solid H_2CO and H + Solid D_2CO

The substitution reactions in formaldehyde were also investigated. Detailed results will be reported elsewhere (Watanabe, Hidaka, & Kouchi 2005, in preparation). Briefly, for D + solid H_2CO , although there is competition between H-D substitution in formaldehyde producing HDCO and D_2CO and the addition of D atoms leading to deuterated methanol, the dominant process is the evolution of $\text{H}_2\text{CO} \rightarrow \text{HDCO} \rightarrow \text{D}_2\text{CO}$ by substitution. It is not clear in the present work whether the substitution proceeds via the sequence of H abstraction and D addition or via H-D direct exchange. The yields of CD_3OD and the other deuterated methanol were small even at the D fluence of $\sim 10^{18} \text{ cm}^{-2}$, indicating that the additions of D to D_2CO , HDCO and H_2CO are slower than substitution. H-D substitution in H_2CO would be an important process to produce deuterated formaldehyde in molecular clouds as much as successive H/D addition to CO.

For H + solid D₂CO, the substitution reaction by H atom (D₂CO → HDCO → H₂CO) proceeded significantly unlike the case of H + solid methanol-*d_n*. The yield of CHD₂OH produced by successive H addition to D₂CO is comparable to that of CH₃OH produced through the route of D₂CO → HDCO → H₂CO → CH₃OH (D-H substitution and subsequent H addition) throughout most of the exposure time. This implies that the rate of H addition to D₂CO is similar to that of D-H substitution (reduction of deuteration level) in D₂CO. The D-H substitution must proceed via sequence of D abstraction and H addition because D-H direct exchange in formaldehyde(-*d_n*) is endothermic.

3.7. D + Solid CD₃OH, CHD₂OH, and CH₂DOH

To determine the relative rates of H-D substitution in methanol-*d_n*, solid CH₃OH, CH₂DOH, and CHD₂OH were exposed to D atoms independently (Nagaoka, Watanabe, & Kouchi 2005, in preparation). Briefly, from the decay curves of parent solids, the relative rates were estimated to be 4, 2, and 1 for CH₃OH → CH₂DOH, CH₂DOH → CHD₂OH, and CHD₂OH → CD₃OH, respectively. The number of H atoms on the methyl side would govern the reactivity.

4. Implications for Astrochemistry

A comparison of the experimental results obtained for H + pure solid CO and CO-H₂O mixed ice with the observational results for molecular clouds is attempted in § 4.1. The potential contribution of the surface reactions of D atoms to the formation of deuterated formaldehyde and methanol is discussed in § 4.2.

4.1. H₂CO and CH₃OH

We compare our results for the hydrogenation of CO-H₂O mixed ice and pure solid CO with the observational results. For instance, assuming that the number density of hydrogen atoms is 1 cm⁻³ and the temperature of the atoms is the same as that of grains in a molecular cloud, the fluences for 10 K are 1.3 × 10¹⁶, 1.3 × 10¹⁷, and 1.3 × 10¹⁸ cm⁻² over 10⁴, 10⁵, and 10⁶ yrs, respectively. In the present experiments, those fluences approximately correspond to 1, 4, and 40 minutes, respectively, at 10 K. The obtained ratios of CO/CH₃OH and H₂CO/CH₃OH are plotted in Figure 4 with the observational abundances. The plots vary from left to right with the decrease in H fluence from 10⁶ to 10⁴ yrs. The leftmost plots correspond to 10⁶ yrs. The results for the higher fluences (10⁶ yrs) are reasonably consistent with the observations of molecular clouds and comets. For pure CO, the data at 12 K is closest to the observations, while the 15 K results are closest for the mixed ice. For both, thinner ice produces higher abundances of CH₃OH relative to the amounts of CO and H₂CO. For thinner ice, the fraction of reactive CO exposed on the surface relative to the fraction of unreactive CO buried in bulk is larger and thus, a ratio of CO/CH₃OH lower than that of thick ice is achieved. The ratio of H₂CO/CH₃OH for pure CO tends to be larger than that for mixed ice at lower ratios of CO/CH₃OH, and this tendency becomes stronger for thinner ice. This feature can be explained by an onion-like structure, as described below. When CO molecules are deposited on the surface, the CO molecules can readily aggregate into bulk (solid) CO even below 1 eML coverage. However, once H₂CO layers have been produced on the solid CO, only the upper layer of the H₂CO can be converted to CH₃OH, resulting in a significant fraction of remnant H₂CO in the bulk. That is, solid CO finally becomes a CO-H₂CO-CH₃OH trilayer structure (Watanabe *et al.* 2004). In the case of mixed ice, CO molecules tend to be isolated in cracks or boundaries of H₂O ice and most of the CO molecules can be finally converted to CH₃OH. The experimental conditions realized

for thinner ice may simulate higher H/CO ratios of accretion onto grains in molecular clouds, where CO always has a chance to react with accreted H atoms at the surface before being buried in bulk.

Our results reveal that the hydrogenation of CO on the grains in a dense core is efficient for the production of H₂CO and CH₃OH regardless of the type of mantle – pure solid CO (apolar ice) or CO-H₂O mixed (polar) ice – as long as the abundance of CO is significant. When CO is abundant in the ice, the competition of H-atom reactions with less abundant species like C₂H₂ and C₂H₄ has little effect on the hydrogenation of CO.

It should be noted that the efficiency of the hydrogenation of CO is strongly dependent on the flux of H atoms; in other words, the number density and kinetic temperature of H atoms and the temperature of the grain. Furthermore, when the photon field of molecular clouds becomes strong, the contribution of photoinduced reactions should be considered. Strictly speaking, these factors should be taken into account.

4.2. H₂CO-*d_n* and CH₃OH-*d_n*

Assuming an H number density of 1 cm⁻³, an atomic D/H ratio of 0.1 in the accreting gas, and that the kinetic temperature of the atoms is the same as that of the grain, the D (H) atom fluences in a 10 K molecular cloud will be 1.3 × 10¹⁶ (1.3 × 10¹⁷), 6.5 × 10¹⁶ (6.5 × 10¹⁷), and 1.3 × 10¹⁷ (1.3 × 10¹⁸) cm⁻² over 10⁵, 5 × 10⁵, and 10⁶ yrs, respectively. In the experiment on H + D + solid CO, these fluences approximately correspond to exposure times of 10, 35, and 70 min, respectively. The ratios of deuterated methanol to the amount of remaining CH₃OH, denoted in the form (CH₂DOH/CH₃OH, CHD₂OH/CH₃OH, CD₃OH/CH₃OH), after exposure times of 10, 35, and 70 min are (0.16, 0, 0), (0.09, 0.05, 0.01) and (0.11, 0.13, 0.03), respectively. These values are markedly consistent with the observations (Parise *et al.* 2004) of (0.3 ± 0.2, 0.06 ± 0.05, 0.014 ± 0.014), indicating that observed deuterium fractionation can be achieved by grain-surface reactions once the atomic D/H ratio of 0.1 in the accretion gas is obtained as suggested by the models. The nondetection of Me-OD is consistent with the low abundance of Me-OD observed toward a low-mass protostar. For formaldehyde, our obtained ratios of (HDCO/H₂CO, D₂CO/H₂CO) are (0.44, 0.034) which are also consistent with the observation of (0.14, 0.05) (Loinard *et al.* 2000). We also performed an experiment with a D/H ratio of 0.05 and found that the results were very similar to those obtained for the ratio of 0.1.

5. Surface Reaction Network for Formaldehyde and Methanol

To date, we have investigated the reactions of hydrogenation, deuteration, and substitution for the systems of solid CO, formaldehyde, and methanol. In Figure 5, a diagram of the surface reaction network for CO, formaldehyde, and methanol is shown with the relative reaction rates estimated so far. Generally speaking, hydrogen addition occurs at a faster rate than deuterium addition due to the effect of the tunneling reaction. The rate constants of hydrogenation and deuteration of CO are higher than those of H₂CO and D₂CO, respectively. An important finding is that *the reaction rates strongly depend on not only the surface temperature but also on the composition and structure of the surface*. For instance, the hydrogenation rate of pure solid CO is different from that of CO in H₂O ice, and H₂CO on solid CO enhances the hydrogenation of CO (Watanabe *et al.* 2005). H-D substitution proceeds for both formaldehyde (H₂CO-*d_n* \xrightarrow{D} H₂CO-*d_{n+1}*; n=0–1) and methanol (CH₃OH-*d_n* \xrightarrow{D} CH₃OH-*d_{n+1}*; n=0–2). There are two possible elementary processes for H-D substitution: direct H-D exchange (e.g., CH₃OH + D → CH₂DOH +

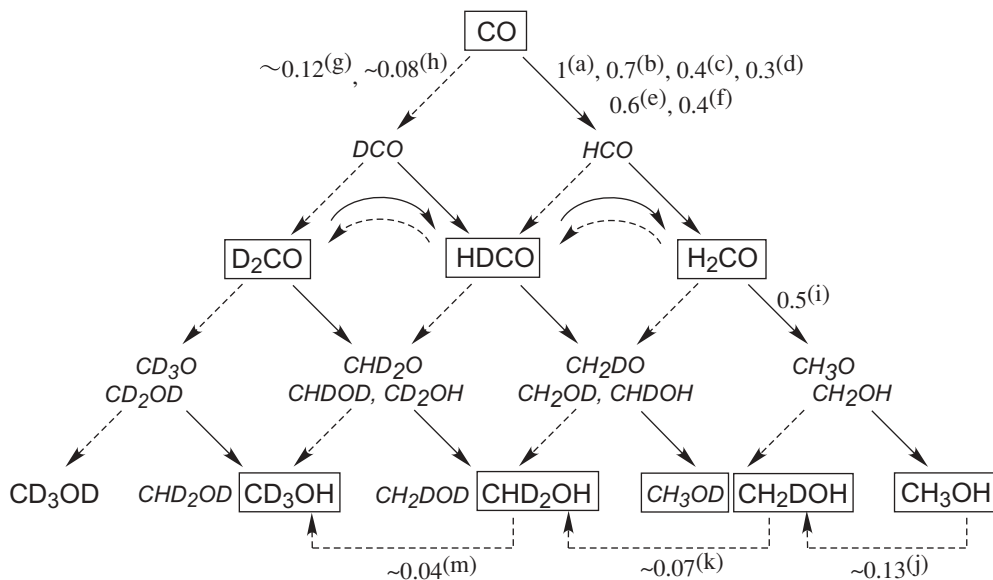


Figure 5. Surface reaction network for CO, formaldehyde, and methanol. Block and italic letters are used to denote products that were detected and not detected in the experiments, respectively. Square frames denote molecules that have been observed in molecular clouds. Solid and dashed arrows represent reactions of H and D atoms, respectively. Although it is likely that abstraction reactions proceed, they are not shown. The values shown are effective rate constants relative to that for H + CO (1 eML) on H₂O (see text) estimated experimentally for the processes represented by the arrows. It should be noted that the effective rate constant strongly depends on the surface composition, structure, and temperature. The values were determined from experiments: (a) H + CO (1 eML) on H₂O at 15 K; (b)–(d) H + CO–H₂O mixed ice at 8, 12, and 15 K, respectively; (e), (f) H + pure CO at 8 and 10 K, respectively; (g) D + CO (1 eML) on H₂O at 15 K; (h) D + pure CO at 10 K. (i) H + H₂CO (1 eML) on H₂O at 15 K; (j) D + pure solid CH₃OH (20 ML) at 10 K; (k) D + pure solid CH₂DOH (20 ML) at 10 K; and (m) D + pure solid CHD₂OH (20 ML) at 10 K.

H) and the sequence of atomic abstraction and addition (e.g., CH₃OH + D → CH₂OH + HD and subsequently CH₂OH + D → CH₂DOH). Although it is not clear which process, the direct exchange or the abstraction-addition, was dominant in our experiments, the activation energies for the latter process is lower than those for the former one (Blowers, Ford, & Masel 1998). For the latter case, H-abstraction/D-addition, the nondetection of Me–OD in the present experiments would be reasonable because H-abstraction in the methyl-side by either H or D has a much lower barrier than in –OH (Kerkeni & Clary 2004).

In contrast, D–H substitution proceeds in formaldehyde (H₂CO–*d*_{*n*+1} $\xrightarrow{\text{H}}$ H₂CO–*d*_{*n*}) proceeds, while that in methanol (CH₃OH–*d*_{*n*+1} $\xrightarrow{\text{H}}$ CH₃OH–*d*_{*n*}) was not observed. For formaldehyde, since the direct D–H exchange (e.g., D₂CO + H → HDCO + D) is endothermic, the combination of D-atom abstraction and H-atom addition is responsible for D–H substitution. For methanol, the direct D–H exchange is also endothermic and, furthermore, an *ab-initio* calculation by Lendvay *et al.* (1997) indicates that the reaction of H-abstraction by H atoms from CH₃OH–*d*_{*n*} (e.g., CH₂DOH + H → CHDOH + H₂) is much faster than that for D-abstraction by H atoms from CH₃OH–*d*_{*n*} (e.g., CH₂DOH + H → CH₂OH + HD). This would be the reason why D–H substitution was not observed.

6. Summary

We have revealed that the hydrogenation of solid CO on grain surfaces can be a major process in the production of H₂CO and CH₃OH in the dense core of molecular clouds where the photon field is very weak. The hydrogenation rates strongly depend on not only the surface temperature but also the composition of the surface. Hydrogenation of CO at 12 K and above is found to be promoted by the coexistence of H₂CO and H₂O molecules on the surface.

The measurements of the deuterium atom exposure of solid CO, formaldehyde, and methanol demonstrated for the first time that deuteration of CO is much slower than hydrogenation of CO and that H-D substitution in solid methanol (methyl side) occurs and acts as a channel for the deuterium fractionation of methanol observed in molecular clouds.

Several effective rate constants for hydrogenation, deuteration, and H-D substitution have been determined to construct the surface reaction network for CO, H₂CO, H₂CO-*d*_n, CH₃OH, and CH₃OH-*d*_n.

References

- Allamandola, L.J., Sandford, S.A., & Valero, G.J. 1988, *Icarus* 76, 225
- Blowers, P., Ford, L., & Masel, R. 1998, *J. Phys. Chem. A* 102, 9267
- Boogert, A. C. A. & Ehrenfreund, P. 2004, in *Astrophysics of Dust*, eds. A.N. Witt, G.C. Clayton, & B.T. Draine (APS Conference Series), Vol. 309, p. 547
- Crovisier, J. & Bockelée-Morvan, D. 1999, *Space Sci. Rev.* 90, 19
- Crovisier, J. *et al.* 2004, *A&A* 418, 1141
- Ehrenfreund, P. & Charnley, S.B. 2000, *ARAA* 38, 427
- Hidaka, H., Watanabe, N., Shiraki, T., Nagaoka, A., & Kouchi, 2004, *Ap. J.* 614, 1124
- Hiraoka, K., Ohashi, N., Kihara, Y., Yamamoto, K., Sato, T., & Yamashita, A. 1994, *Chem. Phys. Lett.* 229, 408
- Hiraoka, K., Sato, T., Sato, S., Sogoshi, N., Yokoyama, T., Takashima, H., & Kitagawa, S. 2004, *Ap. J.* 577, 265
- Ivliev, A. V. *et al.* 1982, *JETP Lett.* 36, 472
- Hudson, R.L. & Moore, M.H. 1999, *Icarus* 140, 451
- Kerkeni, B. & Clary, D. C. 2004, *J. Phys. Chem. A* 108, 8966
- Keane, J.V., Tielens, A.G.G.M., Boogert, A.C.A., Schutte, W.A., & Whittet, D.C.B. 2001, *A&A* 376, 254
- Lendvay, G., Bérces, T., & Márta, F 1997, *J. Phys. Chem. A* 101, 1588
- Loinard, L. *et al.* 2000, *A&A* 359, 1169
- Nagaoka, A., Watanabe, N., & Kouchi, A. 2005, *Ap. J.* 624, L265
- Parise, B. *et al.* 2003, *A&A* 410, 897
- Parise, B. *et al.* 2004, *A&A* 416, 159
- Pontoppidan, K. M., Fraser, H. J., Dartois, E., Thi, W.-F., van Dishoeck, E.F., Boogert, A.C.A., d'Hendecourt, L., Tielens, A.G.G.M., & Bisschop, S.E. 2003, *A&A* 408, 981
- Roberts, H., Herbst, E., & Millar, T.J. 2003, *Ap. J.* 591, L41
- Schutte, W.A., Gerakines, P.A., Geballe, T.R., van Dishoeck, E.F., & Greenberg, J.M. 1996, *A&A* 309, 633
- Shalabiea, O.M. & Greenberg, J.M. 1994, *A&A* 290, 266
- Teixeira, T.C, Emerson, J.P., & Palumbo, M.E. 1998, *A&A* 330, 711
- Tielens, A.G.G.M. & Allamandola, L.J. 1987, in *Interstellar Processes*, eds. D. Hollenbach & H. Thronson (Kluwer, Dordrecht), p. 397
- Tielens, A.G.G.M. & Whittet, D.C.B. 1997, in *Molecules in Astrophysics: Probes & Processes*, ed. E.F. van Dishoeck (Kluwer, Dordrecht), p. 45
- Walraven J.T.M. & Silvera, I.F. 1982, *Rev. Sci. Instrum.* 53, 1167
- Watanabe, N. & Kouchi, A. 2002, *Ap. J.* 571, L173

Watanabe, N., Shiraki, T., & Kouchi, A. 2003, *Ap. J.* 588, L121

Watanabe, N., Nagaoka, A., Shiraki, T., & Kouchi, A. 2004, *Ap. J.* 616, 638

Watanabe, N., Nagaoka, A., Hidaka, H., Shiraki, T., Chigai, T., & Kouchi, A. 2005, *Planet. Space Sci.*, submitted

Discussion

CASELLI: During the experiment, when methanol and deuterated methanol form, is there any evidence of evaporation of a fraction of the formed molecules? This is very important because even a small fraction may solve the problem of methanol formation in the gas phase of dark cold clouds.

WATANABE: I agree about the importance of desorption during the reactions. Unfortunately, we did not measure the desorbed molecules. We can say that more than 90% of the yields remain on the surface, but we do not have clear evidence of desorption in the present experiment. Measurements of desorption caused by reaction will be studied in the future after the modification of our apparatus.

HERBST: What is the fraction of product CH_3OH and CH_3OD that might escape into the gas in your experiments?

WATANABE: We could not detect the CH_3OD product in our experiment on the exposure of solid CH_3OH to D atoms at 10 K. It would be under the detection limit. Activation energies for the abstraction of H atom from the $-\text{OH}$ side by either H and D atoms are much higher than those from methyl group (Kerkeni and Clary 2004). Therefore, the production rates of methyl-OD must be much slower. For desorption, we did not measure the desorbed molecules. So, we do not have direct evidence of the desorption during reactions. Measurements of infrared absorption spectra tell us that the most of products remain in the solid but we do not deny that a small fraction (several percent) of the yield may desorb by the heat of reaction.