Nonenergetic reactions between atomic hydrogen and molecules on interstellar grain surfaces

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Abstract. Reactions of atomic hydrogen with CO and O2 on amorphous solid water (ASW), relevant to chemical evolution on cosmic ice dust, were experimentally investigated at around 10 K. Successive addition of hydrogen atoms to CO and O2 produces H2CO, CH3OH, and H2O2, H2O, respectively. At such low temperatures, some of hydrogen additions such as H + CO → HCO proceed via tunneling reactions rather than thermally-activated reactions. Effective reaction rates and isotope effect of the tunneling reactions to produce HCO and H2O were measured. The surface of ASW was found to enhance the effective rate of hydrogen addition to CO at relatively higher temperatures, namely around 20 K.

1. Introduction

Among the many kinds of interstellar molecules observed, the abundances of some major species such as H2, H2O, and organic molecules can not be explained by pure gas-phase synthesis; therefore, surface reactions on cosmic ice dust are considered for the synthesis of such molecules. In an interstellar molecular cloud where the temperature is as low as 10 K and the radiation field is very weak, the energetic processes in/on ice dust is inefficient and thus tunneling surface reactions involving hydrogen atom become important for chemical evolution in space [1]. Major advantages of dust surface reactions are: since the excess energy of reactions can escape into the surface, recombination and simple addition reactions without dissociation can proceed significantly; because of very low temperatures, most of atoms and molecules stay closely and interact with each other for a long time. These features would enable the efficient synthesis of complex molecules via tunneling reactions, even under the conditions of a molecular cloud. Importance of tunneling reaction on cosmic ice dust was first proposed theoretically in the formation of primordial organic molecules, formaldehyde (H2CO) and methanol (CH3OH) via successive hydrogen atom addition to CO:

\[ \text{CO} \xrightarrow{H} \text{HCO} \xrightarrow{H} \text{H}_2\text{CO} \xrightarrow{H} \text{CH}_3\text{O} \text{(or CH}_2\text{OH)} \xrightarrow{H} \text{CH}_3\text{OH}. \]  (1)

The first and third (radical formation) steps of sequential reaction (1) were reported to have significant activation barriers as high as several hundreds meV [2] and thus require quantum tunneling to proceed at very low temperatures. Furthermore, a recent theoretical model

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predicted that the water molecule, the main component of ice dust, is produced predominantly by the successive addition of O_2:

\[ \text{O}_2 \xrightarrow{H} \text{HO}_2 \xrightarrow{H} \text{H}_2\text{O}_2 \xrightarrow{H} \text{OH} + \text{H}_2\text{O}. \]  (2)

The third step has an activation barrier of \(~400\) meV [3]. In any case, a theoretical approach to the tunneling surface reaction is not easy because the tunneling probability is very sensitive to the structure and composition of the surface. Therefore, experimental studies are desirable.

We present experiments on reactions of hydrogen atoms with O_2 and CO on the ice dust analogue, namely amorphous solid water (ASW), first demonstrating that the abundant molecules in cosmic ice dust, H_2O, H_2CO, and CH_3OH, are efficiently produced via tunneling H-atom addition reactions in interstellar environments.

2. Experimental

The experimental setup and procedure were described in detail elsewhere [4]. The apparatus consists of a hydrogen atomic source and a main chamber. The base pressure of the main chamber is approximately \(3 \times 10^{-10}\) Torr. A mirror-polished aluminum substrate connected to a cold head with a ceramic heater is located at the center of the main chamber. Sample solids were produced on the substrate by vapor deposition through a capillary plate. In the present experiments, solids of CO and O_2 molecules on ASW were exposed to hydrogen atoms. To investigate the isotope effect on reactions, the same measurements were performed with deuterium atoms. The composition and column densities of molecules in solids were measured by infrared reflection absorption spectroscopy. The hydrogen atoms were produced by the dissociation of H_2 molecules in a microwave-induced plasma inside a water-cooled Pyrex tube and thermalized at 100 K by passing through a cold aluminum pipe before impinging on the sample. The atomic fluxes were derived from the changes in the mass readings of mass 1 during the microwave on and off condition. Details of flux estimates are described previously [5]. The typical flux was \(1-5 \times 10^{14}\) cm\(^{-2}\) s\(^{-1}\) with a dissociation fraction of at least 15% [6].

3. Results & Discussion

3.1. H (D) + CO on ASW

When CO on approximately 30 monolayers of ASW (CO-coverage \(\leq 0.1\)) was exposed to H atoms, H_2CO (1178, 1249, 1499, 1722, 2832, 2887, and 2991 cm\(^{-1}\)) and subsequently CH_3OH (1032, 1118, and 2958 cm\(^{-1}\)) were produced with consumption of CO as show in Figure 1 (a). When CO and H_2CO were exposed to H_2 molecules, no reaction was observed. Furthermore, reactions of H_2 with radicals of HCO, CH_3O, and CH_2OH are endothermic [7, 8]. Consequently, the present results clearly demonstrate that H_2CO and CH_3OH are produced by successive H-atom addition (sequential reaction (1)). Reverse processes of sequential reaction (1) reducing the number of H atom by H abstraction were not observed [9, 10]. Intermediate radicals in sequential reaction (1) were not observed, indicating that the first and third steps are the rate-limiting reactions. As soon as radicals HCO and CH_3O (CH_2OH) form, they would be converted immediately to H_2CO and CH_3OH in our high flux condition. Recently, Ioppolo et al. [11] performed a similar experiment and reported the results consistent with ours. In contrast, Zhitnikov and Dmitriev [12] detected HCO but did not detected CH_2OH and CH_3O radicals by ESR in an experiment in which CO gas and H atoms produced by rf discharge were codeposited on a cold quartz finger. Their results imply that under their experimental conditions, the deposited H/CO ratio was significantly low, and thus successive hydrogenation of CO was terminated before the formation of CH_2O or CH_3OH, due to H and HCO being buried in the CO-rich solid.
As described in section 1, the first and third steps in sequential reaction (1) are considered to proceed via tunnelling reactions. To investigate the isotope effect on these tunnelling reactions, we exposed CO on ASW to deuterium (D) atoms. In this measurement, the flux of D atoms was set to be the same as that of H atoms. Figure 1 (b) shows the variation of infrared absorption spectra of the sample upon the D atom exposure. One can see the formation of D\textsubscript{2}CO and CD\textsubscript{3}OD with the consumption of CO, indicating the successive D atom addition to CO as already seen in the H atom experiment. Here we focus on the first step of sequential reaction (1). The reaction rate of the first step can be obtained by the attenuation rates of CO. In Figure 2, the variations in column densities of CO, $\Delta N$(CO) are plotted for the H and D exposure experiments as a function of exposure time. Solid lines are the results of fitting by

$$\frac{\Delta N$(CO)$}{N_0$(CO)$} = \alpha(1 - \exp(-k_{H,D}n_{H,D}t)),$$

where $N_0$(CO) is the initial column density of CO, $N$(CO) is the column density of CO, $n_H$ ($n_D$) is the number density of H (D) atoms at the surface, $k_{H,D}$ is the rate constant for H (D) + CO $\rightarrow$ HCO (DCO), and $\alpha$ is the saturation value. $n_{H,D}$ can be expressed by the balance between the supply of H (D) atoms onto the surface and the losses by H (D) atom desorption, H-H (D-D) recombination, and addition reactions. From the fitting, the ratio of $k_{D}n_{D}/k_{H}n_{H}$ is determined to be 0.08 [5]. Unfortunately, $n_{H,D}$ can not be measured in the present experiments. However, when considering the difference of atomic masses, the loss rate of deuterium adatoms by desorption and reactions would be lower than that of H.
adatoms, leading to the relation of \( n_D \geq n_H \). Therefore, we believe that the obtained value of 0.08 is a higher limit of \( k_D/k_H \).

The above-described experiments were also performed without ASW using pure solid CO. It was found that the surface of ASW enhances the reaction, \( \text{H (D)} + \text{CO} \rightarrow \text{HCO (DCO)} \), significantly at relatively higher temperatures. For \( \text{H} + \text{CO} \) and \( \text{D} + \text{CO} \) at 15 K, the reaction rates on ASW are more than two orders of magnitude larger than those without ASW, that is, on pure solid CO, respectively [1]. The origin of this enhancement due to ASW is not clear. Since the rate of tunneling reaction is closely related to a potential energy surface and residence time of adatoms on the surfaces, the influence of ASW on these factors should be considered. ASW may modify the activation barriers and enhance the tunneling probability, and/or the adsorption energy of H atom onto ASW may be larger than that onto pure solid reactant molecules, that is, the average residence time of adatoms becomes longer on the ASW surface at the higher temperatures. It is plausible that the surface composed of molecules having higher dipole moment produces a higher physisorption energy with H (D) atoms. The dipole moment of \( \text{H}_2\text{O} \) is approximately 20 times larger than that of CO.

3.2. \( \text{H (D)} + \text{solid O}_2 \)
In the experiments on exposure of solid \( \text{O}_2 \) to H atoms, the products of \( \text{H}_2\text{O}_2 \) (3250, 2830, and 1405 cm\(^{-1}\)) and \( \text{H}_2\text{O} \) (3432 and 1650 cm\(^{-1}\)) were obtained as shown in Figure 3 (a). The shape of OH-stretch band (3432 cm\(^{-1}\)) of \( \text{H}_2\text{O} \) clearly shows amorphous but not crystalline structure. This experiment first demonstrates that the water solid produced by surface reactions at very low temperatures becomes the amorphous form consistent with astronomical observations of cosmic ice dust. The formation pathway is considered to be successive H-atom addition (sequential reaction (2)). The intermediate, \( \text{HO}_2 \), was not observed again, indicating that the second step to produce \( \text{H}_2\text{O}_2 \) proceeds much faster than the first step. For D atom exposure, the results were qualitatively the same (Figure 3 (b)). From fitting the data to reaction rate equations, the relative reaction rates of each step in the sequential reaction (2) were determined for both hydrogen and deuterium atoms [13]. The isotope effect was found in only the final step, demonstrating that quantum tunneling dominates the final step. This result accords with theoretical estimates for the activation energies of these reactions in the gas phase. The rate of \( \text{H}_2\text{O} \) formation from \( \text{H}_2\text{O}_2 \) is approximately one and two orders of magnitude larger than that of \( \text{D}_2\text{O} \) and

![Figure 2. Depletion of CO in column density after H (open circle) and D (solid circle) atom exposure at 15 K. Solid lines are results of fitting using equation (3).](image-url)
the depletion rate of CO by H-exposure (HCO formation rate), respectively. In contrast to CO experiments, ASW was found to little enhance reactions of H and D atoms with O2.

Figure 3. Variation of infrared absorption spectra for solid O2 sample due to (a) cold H exposure and (b) D exposure at 10 K. Lines indicate newly formed molecules. Spikes with arrows indicate noise caused by vibration of the He refrigerator.

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