LABORATORY SIMULATION OF D-ENRICHMENT IN INTERSTELLAR FORMALDEHYDE AND METHANOL

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Introduction: Methanol (CH$_3$OH) and formaldehyde (H$_2$CO) are abundant organic species in ice mantle. It has been expected that surface reactions on dusts are necessary to produce the abundant H$_2$CO and CH$_3$OH molecules [e.g., 1]. Our group revealed experimentally that the successive addition of hydrogen atoms to cold solid CO, i.e., CO $\rightarrow$ HCO $\rightarrow$ H$_2$CO $\rightarrow$ CH$_2$O $\rightarrow$ CH$_3$OH, produces H$_2$CO and CH$_3$OH efficiently under the condition of molecular clouds [2-5].

Recently, deuterium enrichments of formaldehyde and methanol were found toward the low mass protostars [6-8] and comet [9]. It is reasonable to expect that the surface reactions play a role in producing deuterated formaldehyde and methanol as well. It is therefore highly desirable to clarify experimentally the role of the surface reactions in D-enrichments.

Using cold atomic hydrogen and deuterium beams, we performed a series of experiments: hydrogenation and deuteration of solid CO, hydrogenation and deuteration of solid H$_2$CO, and deuteration of solid CH$_3$OH.

Experimental: Experiments were performed using the LASSIE and ASURA systems described previously [3-5,10]. The experimental procedure is as follows. An aluminum substrate was placed in the centre of an ultra-high vacuum chamber (10$^{-10}$ Torr) and cooled to 10 K by a helium refrigerator. The solid samples (CO, H$_2$CO, D$_2$CO, and CH$_3$OH) were vapor-deposited on the substrate. The H/D atoms produced by dissociation of H$_2$/D$_2$ molecules by microwave discharge were irradiated to samples. H/D atoms were cooled to 30 K in the atomic source chamber before irradiation. During the irradiation with H/D atoms, we measured the variations of chemical composition of the samples, in-situ, with FT-IR.

Results and discussion: The rate of hydrogenation strongly depends on the surface composition and temperature. The deuteration rate was found to be smaller than hydrogenation rate by a factor of approximately 0.12. This isotope effect can be attributed to the tunneling reaction. In conclusion, the deuteration addition to solid CO (CO + D $\rightarrow$ DCO) would not be the first step to produce the deuterated formaldehyde and methanol.

H$_2$CO was converted to HDCO and D$_2$CO by the reaction with D atom. The conversions to HDCO and H$_2$CO also occur in exposure of D$_2$CO to H atom. The conversion rate to H$_2$CO-D$_{1,2}$ by H$_2$CO + D is faster than that to H$_2$CO-D$_{0,1}$ by D$_2$CO + H. On the other hand, the rate of addition reaction to H$_2$CO by D atom is slower than that rate to D$_2$CO by H atom. Comparing the obtained rates with those for deuteration of CO, we discuss formation route for the deuterated formaldehyde.

It is shown that the H-D substitution in solid CH$_3$OH proceeds more efficiently than successive H and D addition to solid CO to produce deuterated methanol at 10 K [10]. These results indicate a key route for deuteration of methanol on ice dusts, which could explain the observed abundance of deuterated methanol isotopologues in molecular clouds.