Effective rate constants for H-D substitution reactions in methanol on the surface at 10 K

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Recent astronomical observations have discovered extreme deuterium enrichment in interstellar formaldehyde and methanol [1-3]. The abundances of these deuterated molecules are up to 4 orders of magnitude higher than the cosmic D/H ratio of 1.5×10^{-5}. For methanol molecules, even doubly and triply deuterated isotopologues have been detected in the vicinity of low-mass protostars [2,3]. Deuterium fractionation in interstellar molecules has long been a topic of interest in interstellar chemistry, and the fractionation processes in molecular clouds have attracted attention from both astronomers and earth and planetary scientists as a potential explanation for the high D fractionations observed in our solar system. Since pure gas phase chemistry hardly reproduces the deuteration level of formaldehyde and methanol observed, the evaluation of the role of grain surface chemistry in the deuterium fractionation was desirable. For methanol, we recently demonstrated that the H-D substitution reactions in methanol proceed efficiently on the ice surface at 10 K, and that the surface substitution reaction is a key for the deuterium enrichment in molecular clouds [4, 5]. However, the reaction rates of the surface substitution remained to be determined.

To obtained the reaction rates of H-D substitution in (deuterated) methanol on the cryogenic surfaces, solid CH_3OH, CH_2DOH, and CHD_2OH were exposed to D atoms at 10 K. Deuteration levels increased in methyl group in all cases. The pseudo-first-order rates for the reactions $CH_3OH + D \rightarrow CH_2OH + HD$, $CH_2DOH + D \rightarrow CHDOH + HD$, and $CHD_2OH + D \rightarrow CD_2OH + HD$ were estimated. The ratios of the reaction rates of the second and third reactions to the first reaction were 0.69 ± 0.11 and 0.52 ± 0.14, respectively [6]. The difference in reaction rates is thought to be due to a secondary kinetic isotope effect on the H-abstraction reaction from the methyl side by D atoms.

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