HYDROGEN ISOTOPE SUBSTITUTION OF SOLID METHYLAMINE (CH_3NH_2) ON A LOW-TEMPERATURE SURFACE.
Y. Oba[1], N. Watanabe[1] and A. Kouchi[1], [1]Institute of Low Temperature Science, Hokkaido University (N19W8, Kita-ku, Sapporo, Hokkaido 060-0819 JAPAN; oba@lowtem.hokudai.ac.jp.

Introduction: Cometary volatile components are considered to largely originate in molecular cloud (MC) due to similarity in molecular inventory of ices between comets and MC [1]. In addition, volatile molecules in both sources are often enriched in deuterium (D) compared to their terrestrial counterparts, although the degree of D-enrichment significantly varies. For example, the D/H ratio of HCN in comet Hale-Bopp (2.3×10^{-3}) [2] is an order of magnitude larger than that of terrestrial ocean [1], and that of water and organic compounds (i.e. H_2CO and CH_3OH) in low-mass protostars is of the order of 10^{-1}–10^{-2} [3,4]. Laboratory experiments successfully reproduced the observed high D/H ratio of protostar H_2CO and CH_3OH via surface reactions of H or D atoms with CO, H_2CO, and/or CH_3OH at ~10 K [5], which are indicative of the importance of low-temperature surface reactions for D-enrichment in those volatiles.

Methylamine (CH_3NH_2), the simplest alkylamine, has attracted less attention in astrochemistry compared to major molecules shown above. However, it may be an important molecule for the production of amino acid in space due to the structural similarity between them. In fact, it was found that electron irradiation to CO_2/CH_3NH_2 mixed ices yields the simplest amino acid glycine under conditions of interstellar clouds [6]. Moreover, it was recently detected in comet-exposed aerogel fragments returned by Stardust [7], suggesting that CH_3NH_2 may be one of the major components in comet Wild 2. Given the fact that CH_3NH_2 is present in comets, its D/H value may be as high as other cometary molecules like HCN. In that case, the D-enrichment in cometary CH_3NH_2 may originate from chemical reactions in MCs, although deuterated methylamine (e.g. CH_2DNH_2) was not found so far. We investigate the D-substitution reactions of CH_3NH_2 on grain surfaces which may cause its D-enrichment in MCs.

Experimental Details: Experiments were performed in the apparatus named ASURA. The ASURA consists of a main chamber and atomic source. An aluminum substrate was mounted at the center of the main chamber. D atoms were produced by dissociating D_2 in a microwave-induced plasma, and cooled by many collisions with the inner wall of a cold Al pipe (100 K) at the outlet of the source. Solid CH_3NH_2 was produced by the vapor-deposition of gaseous CH_3NH_2 on the substrate at 10–25 K, and was exposed to D atoms for 2 hours. The reaction products were monitored in situ by FTIR.

Results & Discussion: When solid CH_3NH_2 was exposed to D atoms, we observed the formation of deuterated methylamine such as CD_3NH_2 and CD_3ND_2. We assume that a series of H-atom abstraction by D atom and D-atom addition is the dominant process of D-substitution in methylamine. The rate of D-substitution in methyl group (CH_3-) was about 10 times faster than that in amino group (-NH_2) at 10 K. This is attributable to the difference in the activation barrier height for the H-atom abstraction by D atom between CH_3- and -NH_2 [8].

When solid deuterated-methylamine, CD_3ND_2, was exposed to H atoms, H-substitution reactions occurred in both functional groups of CD_3ND_2. The rate of H-substitution was about a factor of two lower than that of D-substitution at 10 K. The fact that H-substitution occurs in both functional groups of methyl amine is strikingly different from the case of methanol. Deuterated methanol like CD_3OD does not react with H atoms [5].

Is methylamine D-enriched in MCs and comets? The fraction of deuterated methylamine would depend on the atomic D/H ratio in environments where it is present. Taking the relative ratio of the rate of D- (k_D) and H- (k_H) substitution reactions ($k_D/k_H \sim 2$ at 10 K) into account, high atomic D/H ratio must be necessary for the significant D-enrichment like H_2CO [4] in MC. Accoding to the deuterium fractionation models in the gas-phase by Roberts et al. [9], the atomic D/H ratio reaches ~0.06 at the later stages (~10^6 years) of molecular cloud evolution. On this basis, we assume that methylamine is possibly enriched in deuterium via surface reactions to some extent in MCs. Accordingly, cometary methylamine could also be D-enriched if it originates in molecular cloud. Further theoretical studies are necessary for more quantitative discussion on the deuteration of methylamine in MCs and comets.

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