MECHANISM FOR THE PREBIOTIC EMERGENCE OF "CHIRALITY": CHIRAL GLYCINE FORMATION ON INTERSTELLAR GRAINS. Y. Oba, N. Watanabe, and A. Kouchi, Institute of Low Temperature Science, Hokkaido University, N19W8, Kita-ku, Sapporo 060-0819 Japan (oba@lowtem.hokudai.ac.jp).

Introduction: Since some kind of chiral molecules has to be formed prior to or at the same time with the emergence of homochirality, we believe that unraveling the origin of chiral molecules is essential to clarify the origin of homochirality. So when and how the first chiral molecule formed in space? We searched for a possibility that some chiral molecules are formed in highly primitive enviroments, namely in interstellar molecular clouds, which are the birthplaces of stars and planets in space. It has been demonstrated that chemical reactions on interstellar grains are of particular importance for the formation and deuterium fractionation of major interstellar molecules such as H_2O and CH_3OH [1-3]. However, there have been no reports on the formation of chiral molecules by surface reactions at ~10 K, which is the typical temperature in molecular clouds.

In the present study, we synthesized chiral glycine ($NH_2CHDCOOH$; d_1-gly) by hydrogen-deuterium substitution of non-deuterated glycine (NH_2CH_2COOH; d_0-Gly) on a cold substrate at ~12 K.

Experimental Methods: All experiments were performed in a reaction apparatus which mainly consists of an ultra-high-vacuum chamber, an atomic source, an effusion cell, and an FTIR spectrometer. The base pressure was of the order of 10^{-7} Pa. d_0-Gly was continuously codeposited with D atoms which were produced by the dissociation of D_2 molecules in microwave induced plasma. Reaction products were extracted from the substrate by H_2O after the codeposition and analyzed by high-resolution mass spectrometry with mass resolution of ~70,000 at m/z = 200.

Results & Discussion: We observed three peaks in the mass spectra of glycine samples at m/z ~ 77, which are derived from $C_2H_5{}^{15}NO_2$, $^{13}CCH_5NO_2$, and $C_2H_4DNO_2$. When d_0-Gly was codeposited with D atoms at 12 K, the peak intensity at m/z = 77.0459 ($C_2H_4DNO_2$) was significantly enhanced, while the relative peak intensity between $C_2H_5{}^{15}NO_2$ and $^{13}CCH_5NO_2$ did not change. This clearly indicates that H-D substitution of d_0-Gly proceeds by the codeposition with D atoms. Since labile hydrogens in d_0-Gly (amino and carboxyl groups) are replaced with those of H_2O (= terrestrial D/H ratio) during sample extraction, the observed $C_2H_4DNO_2$ peak should be attributable to chiral d_1-Gly. The initial ratio of d_1-Gly to d_0-Gly is 7.0×10^{-4} and increases at most to 2.4×10^{-1} under the present experimental conditions.

We propose two-step H-D substation mechanisms for the formation of chiral glycine: H atom abstraction from d_0-Gly by D atom ($NH_2CH_2COOH + D \rightarrow NH_2CHCOOH + HD$), followed by the addition of D atom ($NH_2CHCOOH + D \rightarrow NH_2CHDCOOH$). The first step has a large barrier of about 23.4 kJ mol^{-1} [4]. Since a reaction with such a large barrier does not thermally occur at temperatures as low as 10 K, this reaction should proceed through quantum tunneling.

Astrophysical Implication: Interstellar glycine has been searched extensively; however, it has never been firmly identified by radio telescopes [5]. On the other hand, laboratory experiments demonstrated that glycine can be formed under astrophysically relevant conditions [6]. The present results suggest that the formation of chiral d_1-Gly is favored in dense molecular clouds where D atoms would be much more abundant than d_0-Gly. On this basis, we propose that d_1-Gly dominates over d_0-Gly in molecular clouds and hence we should search for d_1-Gly as well as d_0-Gly by high-performance radio telescopes such as ALMA.

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