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Editors Choice

Chiral glycine formation on cold interstellar grains by quantum tunneling hydrogen–deuterium substitution reactions

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ABSTRACT

We report experimental evidence that chiral glycine ($NH_2CHDCOOH$) is formed by the surface reaction of normal glycine (NH_2CH_2COOH) solid with deuterium (D) atom at 12 K under the simulative conditions of interstellar molecular clouds. Chiral glycine formation is most likely initiated by the tunneling abstraction reaction of H atom by D atom followed by the addition of D atom to the glycine radical ($NH_2CHCOOH$). Given that chiral glycine can form in such a primordial low-temperature environment, it might source molecular chirality as molecular clouds evolve into planetary systems.

1. Introduction

Since the pioneering work of Pasteur 150 years ago, the origin of homochirality in biologically important molecules, such as amino acids and sugars, has been vigorously debated, with no consensus reached to date [1,2]. On the other hand, the origin of chiral molecules per se has been little discussed, probably because chiral molecules are commonplace on Earth. So which chiral molecule first formed in space? Although carbonaceous meteorites contain chiral amino acids and hydroxyl acids [3,4] and a chiral molecule (alpha-aminoethanol: $NH_2CH(CH_3)OH$) is reported to be formed by thermal reactions of NH_3 with CH_3CHO under relatively warm conditions (~120 K) [5], more primitive chiral molecules may have formed inside low-temperature (~10 K) interstellar molecular clouds. Chemical evolution in such cold environments occurs by ion–molecule reactions, photochemical reactions or quantum tunneling reactions on interstellar grains [6–10]. Grain-surface reactions are considered particularly important for the formation of major solid components such as H_2O, H_2CO and CH_3OH [7,8]. However, there have been no reports on the formation of chiral molecules by low-temperature surface reactions.

Here, we will investigate hydrogen–deuterium substitution in glycine (NH_2CH_2COOH), which is the representative achiral amino acid and obviously present in extraterrestrial environments such as comets [11], under the typical conditions of dense molecular clouds. If one of the H atoms bound to the alpha carbon of glycine is replaced with D, the glycine becomes a chiral molecule with R or S configured stereoisomers [12].

Interstellar gas-phase glycine has been intensively searched by radio telescopes, but has not been detected to date [13,14]. However, it can be formed by ultraviolet or cosmic-ray irradiation of interstellar ice analogues, both with [15,16] and without [17–19] acid-hydrolysis of the organic residues at high temperatures (~100 °C). Glycine formation was also confirmed in situ by a combination of reactive ion scattering and low-energy sputtering methods when a CO_2 and CH_3NH_2 mixed ice was photolyzed on an H_2O ice at low temperatures [20]. In addition, experiments and theory predict that gaseous glycine is formed by neutral–neutral and ion–molecule reactions [21,22]. Regardless of the formation mechanism, we expect that glycine resides on the icy surfaces of grains in molecular clouds, whereas other simple chiral amino acids, such as alanine and serine, would be less readily formed on these surfaces [23].

Glycine could exchange its labile hydrogens (carboxyl and amino groups) with deuterium atoms in deuterated species such as HDO and CH_3OD even at low temperatures; however, H–D exchange on the alpha-carbon does not thermally proceeds at temperatures as low as 10 K, which is the typical temperature of molecular clouds. Previous studies demonstrated that carbon-bound hydrogen in some organic molecules can be exchanged with D atoms by reactions with D atoms at such low temperatures [7]. For example, methanol, which is one of the most primordial interstellar organic molecules, exchanges its carbon-bound H with D by the following reactions:

$$CH_3OH + D \rightarrow CH_2OH + HD, \quad (1)$$

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$$CH_2OH + D \rightarrow CH_2DOH. \quad (2)$$

Since reaction (1) does not proceed thermally at ~10 K due to the large barrier, quantum-tunneling is prerequisite for the abstraction of an H atom on cold interstellar grains [7]. Hence, in the present study, we perform laboratory experiments on the formation of chiral deuterated glycine ($NH_2CHDCOOH$) by reacting normal glycine, NH_2CH_2COOH, with D atoms at low temperatures, as well as quantum-chemical calculations on the potential energy surface of the related reactions. Since chiral glycine acts as a recognized catalyst for amplifying an enantiomeric excess under certain conditions [24], the present results could have a potential to contribute to a long standing debate on the origin of homochirality.

2. Experimental

2.1. Experimental conditions

The main components of our experimental apparatus were an ultra-high-vacuum chamber, an atomic source, a Fourier transform infrared spectrometer, and an organic effusion cell. The apparatus is detailed in our previous paper [7]. The base pressure of the apparatus is of the order of 10^{-7} Pa. All reactions were performed on aluminium substrate placed at the centre of the reaction chamber. The reaction temperature was 12 K. Glycine was deposited into an organic effusion cell (KOE-Cell, Kitano Seiki Co., Ltd.) attached to the reaction chamber. Several tens of milligrams of non-deuterated achiral glycine (d_0-Gly, NH_2CH_2COOH, 99%, Kishida Chemical Co., Ltd.) or mono-deuterated glycine (d_1-Gly, $NH_2CHDCOOH$, 98%, SAIL Technologies Inc.) reagents were loaded into a quartz crucible, which was mounted in the heater of the effusion cell. The crucible was heated to 65–90 °C. Once the crucible had reached the desired temperature, the effusion cell was shifted to approximately 5 cm from the substrate, its shutter was opened and the deposition of glycine was commenced. Depending on the cell temperature, the glycine deposition rate ranged from $\sim 3.4 \times 10^{13}$ to $\sim 7.4 \times 10^{14}$ molecules cm^{-2} s^{-1}. The deposition rates were determined from the weight of the deposited glycine, the deposition time and the surface area of the Al substrate. The D_2 molecules were dissociated into D atoms in a microwave-discharge plasma. As the atoms were transferred from the atomic source to the reaction chamber, they were cooled to ~100 K by multiple collisions with the inner wall of the aluminium pipe, which was held at that temperature. The atom temperature is too low to overcome the activation barrier for the reactions studied (Figure 1 and Table 1). The flux of D atoms was estimated as $\sim 6.4 \times 10^{14}$ atoms cm^{-2} s^{-1} using procedure of Oba et al. [25]. Glycine and D atoms were continuously codeposited on the Al substrate for up to 360 min (hereafter, this experiment is denoted as D-only experiment).

We also performed similar experiments where glycine was codeposited with both H and D atoms (H/D-mixing experiment). A gaseous mixture of H_2 and D_2 (H_2/D_2 ratio = 10:1) was prepared in a vacuum line, and the ratio was checked by mass spectrometry using a Granville–Phillips 830 VQM system (MKS Instruments Inc.) attached to the reaction chamber. In the H/D-mixing experiment, the H and D atom fluxes were estimated as $\sim 5.8 \times 10^{14}$ and $\sim 5.8 \times 10^{13}$ atoms cm^{-2} s^{-1}, respectively.

2.2. Analytical procedure

Once the reaction was complete, the sample (up to 500 μg) was dissolved in several tens of microliters of distilled and deionised H_2O at room temperature and atmospheric pressure. The aqueous glycine sample recovered by this process was analysed by high-resolution mass spectrometry using a Thermo Scientific Exactive with mass resolution $m/\Delta m \sim 70\,000$ at mass-to-charge ratio (m/z) = 200 (Thermo Fischer Scientific, Inc.). The basic concept and principle of the mass spectrometer, and examples of its application are described elsewhere [26,27]. A small aliquot of the sample was dissolved in methanol and approximately 5 μl of this solution was introduced into the mass spectrometer by flow injection. The mass spectrum was measured in positive ion mode with a spray voltage of ~3 kV. The capillary voltage and temperature of the ion transfer were 25 V and 300 °C, respectively. The experimental and analytical reproducibility of d_1-Gly/d_0-Gly were within approximately 10% and 5% of the mean, respectively. The main peak was observed at m/z = 76.0397 in positive mode. This value was derived from the m/z of the molecular ion ($C_2H_5NO_2H^+$) of d_0-Gly, calculated as 76.0393.

2.3. Quantum-chemical calculation

The potential energy surfaces of the H or D abstractions from glycine by H or D atoms were calculated using the hybrid density functional B3LYP method. To obtain the molecular structures and zero-point vibrational energies at the energy minima and the transition states on the potential energy surfaces, we adopted a 6-311G(d,p) basis set. The relative energetics were calculated using the CCSD(T) method with the aug-cc-pVDZ basis function [28]. All calculations were conducted using the GAUSSIAN 03 program [29]. The energy diagram of the reactions of d_0-Gly with D atoms is illustrated in Figure 1. The calculated activation barriers and the heats of formation of the reactions as well as the tunneling masses of the reactions are summarised in Table 1.

3. Results and discussion

3.1. Reaction with D atoms

The codeposition of d_0-Gly with D atoms at 12 K yielded d_1-Gly, as evidenced by the largely increased peak intensity of d_1-Gly at m/z = 77.0459 in the high-resolution mass spectra (Figure 2). No reaction occurred when glycine was codeposited with D_2 on the substrate at 12 K, indicating that H–D substitution actually occurred by glycine–deuterium reactions. Here, the d_1-Gly was detected as a protonated molecular ion, $[C_2H_4DNO_2+H]^+$ (calculated m/z = 77.0456). The abundance of d_1-Gly relative to d_0-Gly (d_1-Gly/d_0-Gly) in the sample was initially 7.0×10^{-4}, increasing to 5.1×10^{-2} and 2.4×10^{-1} following codeposition at d_0-Gly–atom flux ratios (denoted by F_{gly}/F_{atom}) of ~1.2 and $\sim 5.3 \times 10^{-2}$, respectively. Monodeuterated glycine, wherein one carbon is replaced with ^{13}C ($[^{12}C^{13}CH_4DNO_2+H]^+$: calculated m/z = 78.0489), and dideuterated glycine (d_2-Gly, $[C_2H_3D_2NO_2+H]^+$: calculated m/z = 78.0519) were also observed at m/z = 78.0493 and 78.0521, respectively (Figure 3), although these are minor products compared with d_1-Gly. No tri, tetra or pentadeuterated glycine was identified in the mass spectra of any sample.

When extracted from the substrate, glycine readily exchanges its labile hydrogens (two in the amino group and one in the carboxyl group) with those of excess H_2O. Moreover, the aqueous glycine sample was dissolved in excess methanol during the analysis with the high-resolution mass spectrometer. Therefore, although the H atoms could be replaced with D atoms during the experiment, the D/H ratios of both carboxyl and amino groups are of order 10^{-4} (their terrestrial values). However, in the present experiment, the relative abundances of d_1- and d_2-Gly increased following the reaction with D atoms (Figures 2 and 3), indicating that one or two of the carbon-bound hydrogens had been replaced by D atoms and not exchanged with H atoms in water and methanol.

We propose a two-step mechanism of the H–D substitution of glycine: first, an H atom is abstracted by a D atom