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Deuterium fractionation during amino acid formation by photolysis of interstellar ice analogs containing deuterated methanol

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ABSTRACT

Deuterium (D) atoms in interstellar deuterated methanol might be distributed into complex organic molecules through molecular evolution by photochemical reactions in interstellar grains. In this study, we use a state-of-the-art high-resolution mass spectrometer coupled with a high-performance liquid chromatography system to quantitatively analyze amino acids and their deuterated isotopologues formed by the photolysis of interstellar ice analogs containing singly deuterated methanol CH_2DOH at 10 K. Five amino acids (glycine, α-alanine, β-alanine, sarcosine, and serine) and their deuterated isotopologues whose D atoms are bound to carbon atoms are detected in organic residues formed by photolysis followed by warming up to room temperature. The abundances of singly deuterated amino acids are in the range of 0.3–1.1 relative to each nondeuterated counterpart, and the relative abundances of doubly and triply deuterated species decrease with an increasing number of D atoms in a molecule. The abundances of amino acids increase by a factor of more than five upon the hydrolysis of the organic residues, leading to decreases in the relative abundances of deuterated species for α-alanine and β-alanine. On the other hand, the relative abundances of the deuterated isotopologues of the other three amino acids did not decrease upon hydrolysis, indicating different formation mechanisms of these two groups upon

hydrolysis. The present study facilitates both qualitative and quantitative evaluations of D fractionation during molecular evolution in the interstellar medium.

Key words:

astrochemistry − ISM: clouds − ISM: molecules − molecular processes

1. INTRODUCTION

The deuterium (D) enrichment of methanol (CH_3OH) observed in the interstellar medium is outstanding in terms of the abundances and types of deuterated isotopologues among interstellar molecules observed thus far. For example, the singly deuterated isotopologue CH_2DOH has been observed toward the star-forming region IRAS 16293-2422, whose abundance is ~90% of CH_3OH (Parise et al. 2002). Moreover, triply deuterated methanol CD_3OH has been detected in the same region (Parise et al. 2004). Because such a high degree of D enrichment, especially for multiply deuterated methanol such as CD_3OH, cannot be reproduced by ion–molecule reactions in the gas phase, grain-surface reactions are necessary to explain the observed high abundances of deuterated methanol isotopologues. Laboratory experiments have successfully reproduced high degrees of D enrichment in solid methanol through quantum-tunneling

hydrogen–deuterium (H–D) substitution reactions at 10 K (Nagaoka et al. 2005, 2007).

Methanol plays a role as an important precursor for complex organic molecules (COMs) via photochemical reactions in interstellar icy grains. Öberg et al. (2009) clearly demonstrated that the photolysis of solid CH_3OH layers resulted in the formation of various COMs such as dimethyl ether (CH_3OCH_3) and methylformate ($HCOOCH_3$). In addition, the formation of astrobiologically important molecules such as amino acids (AAs) and sugars has been demonstrated in numerous laboratory experiments in which ice mixtures containing not only CH_3OH but also H_2O and NH_3 were photolyzed at low temperatures followed by warming up to room temperature (Bernstein et al. 2002; Muñoz Caro et al. 2002; de Marcellus et al. 2015; Meinert et al. 2016).

Given that deuterated methanol formed on grains by an H–D substitution reaction undergoes molecular evolution as a result of photochemical reactions in the interstellar medium, D atoms in deuterated methanol should be distributed in the aforementioned “daughter” molecules such as AAs and sugars to some extent. The understanding of D fractionation between parent and daughter molecules has significant potential as a tool for pursuing molecular evolution from dense molecular clouds to planetary systems. However, this topic has not been considered in previous studies. This may be partly because of the difficulty involved in quantitatively measuring the

abundances of deuterated species using pre-existing analytical methods.

We recently succeeded in quantitatively measuring the abundances of simplest AA glycine (NH_2CH_2COOH) and its deuterated isotopologues ($NH_2CHDCOOH$ and NH_2CD_2COOH) at an isotopologue level using a state-of-the-art high-resolution mass spectrometer based on the exact masses of these molecules (Oba et al. 2015). Although glycine was a sole analyte in our previous study, we are confident that this technique is applicable to the analysis of a complex mixture of organic molecules utilizing a chromatographic separation technique with high-performance liquid chromatography (HPLC). In the present study, we quantitatively analyzed the D enrichment of AAs formed by the photolysis of interstellar ice analogs containing deuterated methanol, CH_2DOH.

2. EXPERIMENTS

The photolysis of interstellar ice analogs was performed using the setup for analysis of molecular and radical reactions of astrochemical interest (SAMRAI). SAMRAI mainly consists of an ultra-high-vacuum reaction chamber, a Fourier transform infrared spectrometer (FTIR), a quadrupole mass spectrometer, and turbomolecular pumps. The base pressure is on the order of 10^{-7} Pa. Two D_2 discharge

lamps (L12098; Hamamatsu Photonics), whose photon flux is on the order of ~10^{13} photons cm^{-2} s^{-1}, are attached to the reaction chamber. The wavelength of UV photons is 115–170 nm and has two peaks at ~121 and ~160 nm. An Al substrate connected to a He refrigerator is placed at the center of the reaction chamber. Gaseous samples containing H_2O, CO, NH_3, and CH_2DOH with a mixing ratio of 5:2:2:2 were prepared in a sample preparation chamber and continuously deposited onto the Al substrate at 10 K through a capillary plate at a total gas flow of ~10^{13} molecules cm^{-2} s^{-1}. The samples were then exposed to UV photons throughout the deposition periods of up to 200 hr. After simultaneous gas deposition and photon irradiation, the substrate was warmed to room temperature to eliminate volatile species, and the formation of solid organic residues was confirmed by FTIR (Figure 1). The most noticeable feature on this spectrum is the presence of a strong C–D stretching band at ~2200 cm^{-1}, which was not observed in the related previous studies that did not use deuterated species as a parent molecule (e.g. Bernstein et al. 1995; Muñoz Caro et al. 2004). These organic residues were extracted from the substrate by dissolving it in several tens of microliters of water/methanol mixture (1/1 by volume). To obtain sufficient amounts of reaction products for further quantitative analyses, four trials of the same experiment were performed and extracts in each run were combined into one solution. Half of the

solution was analyzed using the high-resolution mass spectrometer without further chemical treatment, and the other half was hydrolyzed in 6 M HCl at 110 °C for 12 hr, followed by acid removal for further analysis using the mass spectrometer. Each sample was once dried and dissolved in distilled and deionized water (1 ml). The nonhydrolyzed and hydrolyzed samples are hereafter denoted as “free” and “bound” samples, respectively.

Five microliters of each solution were injected into a mass spectrometer (Q Exactive Focus; Thermo Fischer Scientific) with a mass resolution $m/\Delta m$ ~ 70,000 at a mass-to-charge ratio (m/z) = 200 through an HPLC system (UltiMate 3000; Thermo Fischer Scientific) equipped with a Hypercarb separation column (4.6 × 150 mm, 5 μm i.d.; Thermo Fischer Scientific). The detailed conditions of HPLC analysis are described elsewhere (Takano et al. 2015). The mass spectrum was recorded in the positive electrospray ionization mode with an m/z range of 70–350 and a spray voltage of 3.5 kV. The injected samples were vaporized at 300 °C. The capillary temperature of the ion transfer was 300 °C. The same volume of distilled water was measured to check the contamination level of the mass spectrometer; however, no AA was detected during the measurement.

3. RESULTS

Owing to the coupled use of the high-resolution mass spectrometer and HPLC, we successfully detected five AAs and their deuterated isotopologues in the reaction products: glycine (Gly: NH_2CH_2COOH), α-alanine (αAla: $NH_2CH(CH_3)COOH$), β-alanine (βAla: $NH_2CH_2CH_2COOH$), sarcosine (Sar: CH_3NHCH_2COOH), and serine (Ser: $NH_2CH(CH_2OH)COOH$). The molecular structures of these AAs are shown in Figures 2–4. The validity of these assignments was checked by a comparison with the retention index of the molecules in question under the same analytical conditions (Takano et al. 2015) and using a different method following Zhang et al. (2012).

Under the present analytical conditions, hydrogen atoms in polar functional groups such as amino and carboxyl groups are easily exchanged with those of solvents such as methanol and water (D/H ~1×10^{-4}). Therefore, all D atoms in the identified deuterated isotopologues should be bound to carbon atoms because such D atoms do not easily exchange with ambient H atoms (Oba et al. 2015). Hereafter, AA isotopologues are denoted as d_n-*X*, where *n* and *X* represent the number of D atoms in a molecule and the abbreviation of the AA (*X* = Gly, αAla, βAla, Sar, or Ser), respectively.

3.1. Glycine

Figure 2a shows the mass chromatograms of free and bound samples as well as that of a d_0-Gly standard reagent (std) at an *m/z* value of 76.0393, corresponding to the mass of protonated d_0-Gly ($C_2H_5NO_2H^+$). Multiple peaks were observed in the mass chromatograms of both samples, which suggest the presence of structural isomers of d_0-Gly in the reaction products. By comparing retention times between d_0-Gly std and the reaction products, the peak at ~17.8 minutes of both reaction products was assigned to d_0-Gly. Among the five AAs, Gly was the most abundant in both samples and the concentration of d_0-Gly in the bound sample was ~13 times greater compared with the free counterpart (Table 1). These results agree well with those of previous studies (Nuevo et al. 2008).

Figure 2b shows the mass spectra of the peak at 17.8 minutes for the d_0-Gly std and both samples at *m/z* values of 75.5–79.5. The most intense peak was observed at *m/z* ~ 76.0394 in the three mass spectra, which is attributable to d_0-Gly. In addition, in the mass spectra for both reaction products, two small peaks were observed at *m/z* values of 77.0456 and 78.0518, corresponding to d_1-Gly and d_2-Gly, respectively. The relative abundances of d_1-Gly (d_1-Gly/d_0-Gly) and d_2-Gly (d_2-Gly/d_0-Gly) were ~0.3 and ~0.01, respectively, for both samples.

3.2. α-alanine, β-alanine, and Sarcosine

Figure 3a shows the mass chromatograms of the three AA stds (αAla, βAla, and Sar), and the free and bound samples at an *m/z* value of 90.0550, which corresponds to that of protonated ions. Various peaks were observed for both the free and bound samples. By comparing the retention times and indices of the observed peaks, we selected three peaks corresponding to Sar, αAla, and βAla in both reaction products. This assignment was confirmed to be appropriate by an additional analysis of the samples coinjected with an internal std. Earlier elution of the three AAs compared to the stds may have been due to a matrix effect of complex organic residues in both samples and/or isotope effects between the sample and stationary phase of the separation column (Filer 1999). To the best of our knowledge, this is the first detection of β-alanine and sarcosine in similar organic residues without acid hydrolysis. Among these three isomers, in the free sample, we found that β-alanine was the most abundant, followed by sarcosine (~64% of β-alanine) and α-alanine (~39%). In the bound sample, α-alanine was the most abundant, followed by sarcosine (~76% of α-alanine) and β-alanine (~45%). Note that the abundances of alanine isomers increased after acid hydrolysis by a factor of more than five, similar to the case of glycine.

Deuterated isotopologues of αAla, βAla, and Sar were also observed in the

mass spectra (see Figure 3b for Sar as an example). As presented in Table 1, the relative abundances of d_1–d_3 species (e.g., d_1-Sar/d_0-Sar, d_2-Sar/d_0-Sar, and d_3-Sar/d_0-Sar, respectively) for the three AAs in the free sample were 0.8–1.1, 0.2–0.4, and 0.004–0.04, respectively. After hydrolysis, the relative abundances of the d_1–d_3 species for Sar changed little, similar to Gly, compared to those in the free sample. On the other hand, this is not the case for αAla and βAla; the relative abundances of their d_1–d_3 species significantly dropped (<60%) compared to those in the free sample. The reason for this observation is discussed later in detail.

3.3. Serine

Figure 4 shows mass chromatograms at m/z = 106.0499 (which corresponds to the protonated d_0-Ser) for the free sample, a d_0-Ser std, and a mixture of both at an appropriate ratio. In the case of d_0-Ser, a comparison of the retention times did not lead to a reliable assignment of the molecule, similar to the case of alanine isomers. Based on coinjection analysis (Figure 4c), the most intense peak at ~19.8 minutes in the mass chromatogram of the free sample was found to be d_0-Ser (Figure 4a). Earlier elution of d_0-Ser in the free sample compared to the standard reagent probably occurred for the same reasons as those in the case of Sar and its structural isomers. We also detected

d_0-Ser in the bound sample (not shown), whose abundance was one order of magnitude higher than that in the free counterpart. Among the five AAs, serine was the least abundant identified in both free and bound samples.

Singly and doubly deuterated serine isotopologues (d_1-Ser and d_2-Ser, respectively) were detected in both free and bound samples. The relative abundances of d_1-Ser and d_2-Ser in the free sample were consistent with those in the bound sample (d_1-Ser/d_0-Ser = ~0.5 and d_2-Ser/d_0-Ser = ~0.07), similar to the cases of glycine and sarcosine (Table 1).

4. DISCUSSION

4.1. Deuterium Fractionation Pathways

Because CH_2DOH is the only molecule among the reactants to contain a D atom, D atoms in the reaction products should originate from CH_2DOH. It is well known that there are several photodissociation channels of methanol depending upon the wavelength of UV photons (Hama et al. 2009; Öberg et al. 2009). The representative channels in the case of CH_2DOH at the present photon wavelengths are as follows:

$$CH_2DOH \rightarrow CH_2D + OH, \quad (1)$$

$$CH_2DOH \rightarrow CH_2OH + D, \quad (2a)$$

$CH_2DOH \rightarrow CHDOH + H,$ (2b)

$CH_2DOH \rightarrow CH_2DO + H.$ (3)

If CH_2D and CH_2DO radicals formed by reactions (1) and (3), respectively, were directly incorporated into AAs, they should have at least one methyl group with a D atom. In that case, nondeuterated isotopologues would not be produced; however, they are actually observed in the reaction products (Table 1). In addition, methyl groups are not necessarily present in the produced AAs such as Gly and βAla, implying that reactions (1) and (3) do not have a significant contribution under the present experimental conditions. Öberg et al. (2009) discussed the branching ratio of reactions (1)–(3) in their experiments on the photolysis of pure solid CH_3OH at 20 K; reactions (1):(2):(3) = <1:5 ± 1:1, which indicate that the formation of methyl (CH_2D) and methoxy (CH_2DO) radicals is less favored than that of CH_2OH (CHDOH). These results do not qualitatively contradict those of our experiment. If CH_2OH radicals are preferentially used for AA formation, deuteration levels should decrease. In fact, the nondeuterated species are the most abundant in four of the five AAs detected (Table 1), which agrees well with the assumption.

In addition to the reactions presented above, the following unimolecular hydrogen molecule elimination (UHME) process may occur during the photolysis of

methanol at low temperatures (Gerakines et al. 1996; Hama et al. 2009):

$CH_2DOH \rightarrow CDOH + H_2$, (4a)

$CH_2DOH \rightarrow CHOH + HD$, (4b)

$CH_2DOH \rightarrow HDCO + H_2$, (5a)

$CH_2DOH \rightarrow H_2CO + HD$. (5b)

The reaction products of UHME process may be incorporated into AAs. If these reactions occur in a statistical manner, the frequencies of reactions (4b) and (5a) are twice as large as those of their counterparts (reactions 4a and 5b, respectively) because the number of C–H bonds in CH_2DOH is larger than that of the C–D bond, which may affect the D/H ratio of the reaction products.

The production of C–H bonds is also possible from other pathways that do not use methanol as a reactant. Briggs et al. (1992) reported the formation of various COMs such as glycolic acid ($HOCH_2COOH$), glycerol ($HOCH_2CH(OH)CH_2OH$), and Gly after the photolysis of solid mixtures ($CO:H_2O:NH_3$ = 5:5:1) at 10 K. Although their gas composition is different from that in our study, similar products can be produced in the present experiment, which has the potential to decrease the deuteration level of Gly. Although the formation of other AAs was not reported by Briggs et al., others reported the formation of various AAs upon the hydrolysis of the organic residues even in the

absence of methanol (Muñoz Caro et al. 2002), which should have the potential to drastically decrease their deuteration levels.

4.2. Effect of Hydrolysis on Deuteration Levels of Amino Acids

We demonstrated that the acid hydrolysis of the organic residues generally results in significant increases in AA abundances, which is consistent with that demonstrated in previous studies (Nuevo et al. 2008; Evans et al. 2012). On the other hand, there has been no report on the variation in the deuteration levels of AAs after the acid hydrolysis of the organic residues. The present result suggests that the five AAs can be divided into two groups depending on whether the deuteration level decreases upon hydrolysis: those whose D/H is significantly decreased (α-Ala and β-Ala; referred to as the Ala group) and those whose D/H did not change (Gly, Sar, and Ser; referred to as the Gly group). This indicates that the two groups have different formation mechanisms upon hydrolysis. We propose one possible scenario to explain the observed D/H ratio: we assume that these five AAs are produced by reactions of small radicals during warming of the irradiated ice and that most AAs formed are incorporated into macromolecules via relatively weak bonds such as peptide bonds. Upon hydrolysis, these weak bonds are broken and the unit AAs are released. If this is the only pathway

for the formation of AAs, the deuteration levels of the AAs would not vary between the free and bound samples, as is the case for Gly-group AAs. On the other hand, for Ala-group AAs, if there are other formation pathways that do not use deuterated radicals and/or molecules upon hydrolysis, the deuteration level would decrease.

We understand that the actual formation pathways of AAs in both free and bound samples as well as their D fractionation pathways discussed in section 4.1 are not as simple as those proposed in our study. Nevertheless, we believe that a detailed analysis of the D/H ratio of AAs formed by the photolysis of interstellar ice analogs is very helpful for deciphering their formation and D fractionation mechanisms.

4.3. Astrophysical and Meteoritic Implications

Although high-resolution mass spectrometry has a powerful potential to detect numerous number of species in a complex mixture of organic molecules such as meteoritic organic compounds (Schmitt-Kopplin et al. 2010) and photochemically produced organic residues (Danger et al. 2013), it is not possible to assign a specific molecule without a chromatographic separation, especially when it has various kinds of structural isomers. In this regard, a recent detection of Gly in the coma of comet 67P/Churyumov–Gerasimenko (Altwegg et al. 2016) is not yet convincing because the

assignment is based on the mass of the observed peak only. In the present study, using a combination of an HPLC with a high-resolution mass spectrometer, we successfully identified Gly in the photochemically produced organic residue (Figure 2a). In addition, we found in the mass chromatogram at m/z = 76.0393 the presence of the other structural isomers whose peak intensities are equivalent to or stronger than that of Gly (Figure 2a), indicating that Gly is not a dominant structural isomer of $C_2H_5NO_2$ in the free sample particularly. Possible candidates for other $C_2H_5NO_2$ isomers could be methylcarbamic acid ($CH_3NHCOOH$) and glycolamide (NH_2COCH_2OH), both of which are reported to be formed under astrophysically relevant conditions (Takano et al. 2004; Bossa et al. 2008).

The D/H ratio of the parent molecules is calculated by the relative abundances and the number of H and D atoms of each molecule (H_2O:CO:NH_3:CH_2DOH = 5:2:2:2) to be 1/11 or ~0.09. If this D/H ratio is statistically inherited to the formed AAs, the d_1-Gly/d_0-Gly and d_1-Sar/d_0-Sar ratios are, for example, calculated to be 0.2 and 0.5, respectively, given the fact that a D atom is bound to a C atom only as explained earlier. Note that these calculated d_1/d_0 values for all AAs detected in the present study are generally lower than those obtained in the present experiment (e.g. ~0.3 and 1.1 for Gly and Sar, respectively; Table 1) by a factor of up to ~2, which means that the relative

abundance of deuterated isotopologues cannot be explained by a statistical behavior. This is probably because the C–D bond in the parent CH_2DOH molecule partly remains undissociated during photolysis and is to some extent inherited to the formed AAs.

A diverse suite of AAs has been found in carbonaceous meteorites, which are the most primitive solar system materials (Pizzarello & Huang 2005; Pizzarello et al. 2008; Burton et al. 2012). D enrichments of meteoritic AAs have been considered as clear evidence for their formation in extraterrestrial environments (e.g. Epstein et al. 1987; Pizzarello et al. 1994); however, their decisive formation mechanisms remain unclear. We found that the deuteration levels of the formed AAs tend to increase with the number of C–H bonds in a normal molecule ($N_{C–H}$). $N_{C–H}$ is the largest for Sar ($N_{C–H}$ = 5), which has the largest d_1/d_0 value among the five AAs detected; on the other hand, Gly, which has the smallest $N_{C–H}$ (=2), has the lowest d_1/d_0 ratio (Table 1). This may be a reasonable result for AA formation under D-enriched conditions because molecules should have more chances to incorporate D atoms into themselves as $N_{C–H}$ increases. Note that the D/H ratio of the meteoritic AAs shows a similar trend (Pizzarello & Huang 2005; Pizzarello et al. 2008). In addition, the abundance of the meteoritic AAs is known to increase upon the hydrolysis of water extracts from meteorites, which is similar to the case where the abundance of AAs increases upon the hydrolysis of the organic residues

produced in the laboratory (Nuevo et al. 2008). Both similarities imply a potential link between meteoritic and photochemically produced AAs.

The deuteration levels of AAs in the organic residues would vary depending on the relative abundances of deuterated precursor molecules. Because we used CH_2DOH only as an isotopologue of methanol, the deuteration levels of products were reasonably high. However, in the interstellar medium, normal methanol (CH_3OH) is generally the most abundant, followed by deuterated methanol isotopologues such as CH_2DOH and CD_3OH with different abundances (Parise et al. 2002, 2004). Under these situations, the deuteration levels of the formed AAs are strongly expected to be lower than those measured in the present study. In addition, the duration of photolysis might be very long in the present study (~200 hr, which correspond to 10^8-10^9 years in dense clouds assuming the photon flux of 10^3 photons cm^{-2} s^{-1}, Prasad & Tarafdar 1983) to simulate photochemical reactions in these environments, which may affect the deuteration levels of AAs. To better simulate photochemical reactions in dense clouds, the photon fluence and molecular and isotopic compositions of ice should be better adjusted to the actual conditions in future studies. In addition, isotopic analyses of AAs with more than four carbon atoms and those of other astrobiologically important molecules such as ribose (Meinert et al. 2016) formed by the photolysis of interstellar ice analogs are highly

necessary for better understanding the flow of D during chemical evolution in space, although ribose was not detected among the present organic residues. Nevertheless, the present study facilitates both qualitative and quantitative evaluations of D fractionation during molecular evolution in the interstellar medium.

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Table 1. Concentrations and relative abundances of d_1, d_2, and d_3 isotopologues of five amino acids in free and bound samples.

AAs	Concentration of d_0 Isotopologue (nmol/5μl)	Relative Concentration (Gly = 1)	d_1/d_0	d_2/d_0	d_3/d_0
Free					
Glycine	0.33	1	0.31	0.010	ND*
α-Alanine	0.055	0.17	0.81	0.25	0.004
β-Alanine	0.14	0.42	0.91	0.21	0.02
Sarcosine	0.090	0.27	1.1	0.38	0.04
Serine	0.040	0.12	0.53	0.062	ND
Bound					
Glycine	4.4	1	0.29	0.015	ND
α-Alanine	1.7	0.39	0.30	0.047	0.003
β-Alanine	0.76	0.17	0.52	0.10	0.01
Sarcosine	1.3	0.30	1.1	0.36	0.05
Serine	0.39	0.090	0.53	0.083	ND

*ND: Not detected.

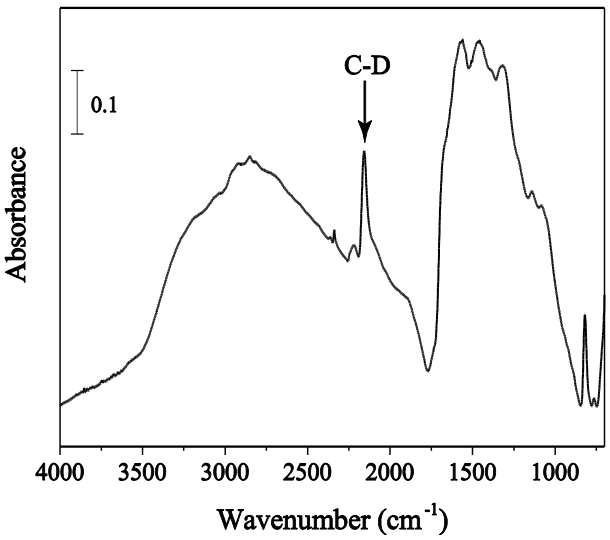

Figure 1. FTIR spectrum of organic residue formed after photolysis of interstellar ice analogs for ~200 hr at 10 K, followed by warming up to 280 K.

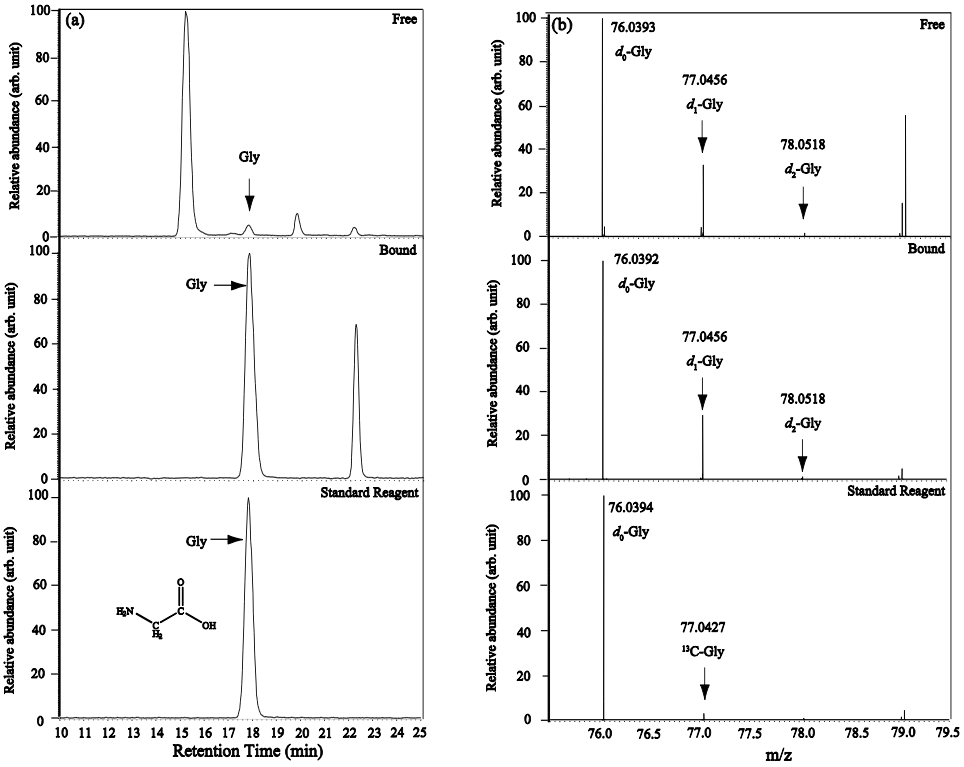

Figure 2. (a) Mass chromatograms of free (top) and bound (middle) samples, the d_0-Gly std (bottom) at *m/z* = 76.0363, and (b) the mass spectrum of each sample at retention time = 17.8 minutes. ^{13}C-Gly represents glycine with one ^{13}C atom instead of ^{12}C.

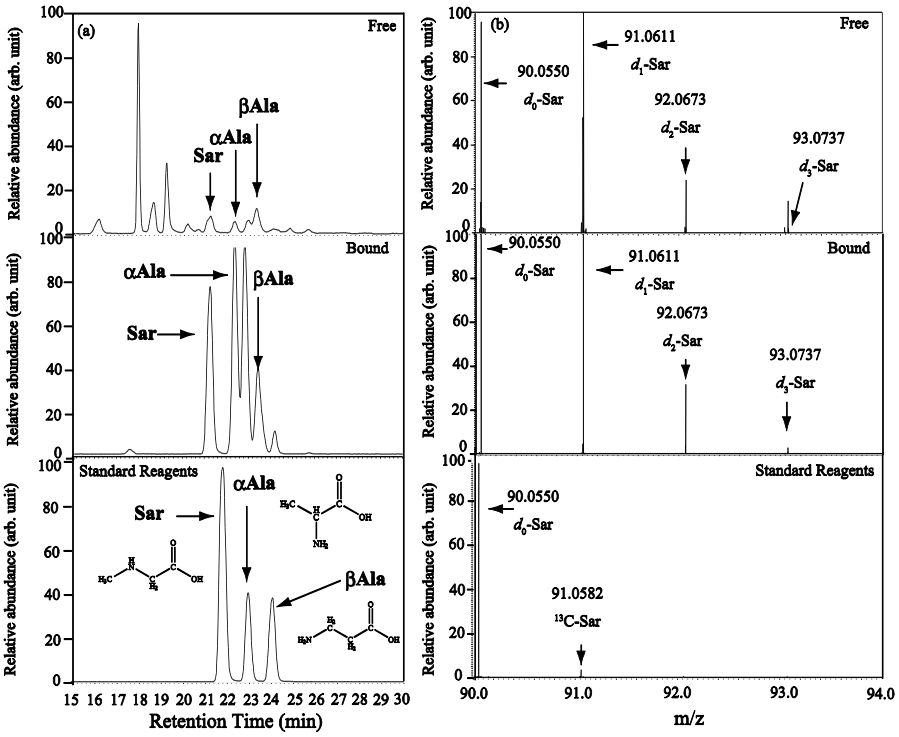

Figure 3. (a) Mass chromatograms (15–30 minutes) of free (top) and bound (middle) samples, the standard reagents of alanine isomers (bottom) at *m/z* = 90.0550, and (b) the mass spectra of Sar at ~21 minutes in the mass chromatogram of each sample. ^{13}C-Sar represents a sarcosine molecule having one ^{13}C atom instead of ^{12}C.

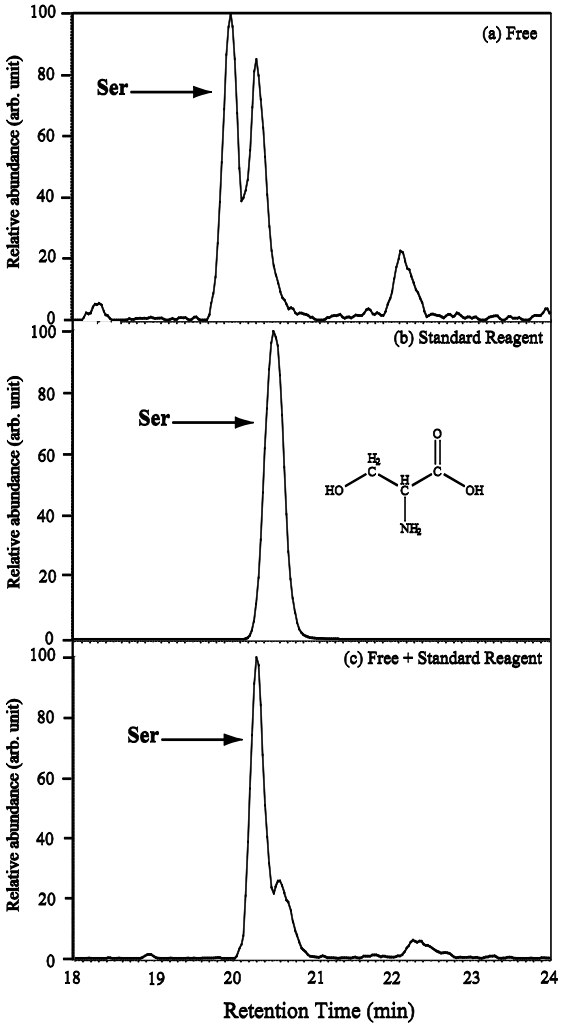

Figure 4. Mass chromatograms of (a) free sample, (b) d_0-Ser std, and (c) mixture of free sample and d_0-Ser std.