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Radiation-induced chemical evolution of biomolecules

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ABSTRACT

Chemical evolution in glycilglycine (Gly2) films irradiated with 146 nm vacuum ultraviolet light was studied. It is found that quantum efficiency of chemical evolution from Gly2 to glycilglycilglycine (Gly3) is smaller than that to glycilglycilglycilglycine (Gly4) due to the multiple step of reaction. Furthermore, we have carried out measurement of soft X-ray natural circular dichroism spectra for serine and alanine films in the energy region of oxygen 1s transition and we report the splitting of 1s→π* transitions.

1. Introduction

Amino acids were detected from some meteorites (Shimoyama et al., 1979), which implies that amino acids were formed in space environment. It is reasonable to assume that radiation in space environment played an important role in chemical evolution (Raulin et al, 2000). Standing on this point of view, it is of interest to study the next stage of chemical evolution, that is, from amino acids to oligopeptides or peptides. It is important for amino acid molecules to get not only the bigger size, but also to get the higher enantiomeric degree toward the final goal of homochirality which is a characteristic nature of biomolecules on the earth. Here we report our recent achievement in studies of oligopeptide formation induced by vacuum ultraviolet (VUV) radiation and the new results of the soft X-ray circular dichroism of amino acids.

2. Oligopeptide formation induced by 146 nm vacuum ultraviolet radiation

Soft X-ray and vacuum ultraviolet radiations are known to induce the condensation reaction of amino acids in solid phase (Kaneko et al., 2005; Tanaka et al., 2008). The papers reported that glycilglycine (abbreviated as Gly2 hereafter) were formed in the vicinity of surface of amino acid films, and fragment species, such as CH_3, CH_4, and NH_3, were easily desorbed from the surface into vacuum during irradiation. Kaneko et al. (2005) reported that, after irradiation of 1.5×10^{15} photons of soft X-ray to solid glycine surface, Gly2 were accumulated on the surface up to 31% due to low vapor pressure of Gly2 and desorption of small fragment species during the mesurement of fine structures in soft X-ray absorption spectra (NEXAFS spectra) of the Gly solid. As a next stage of chemical evolution by starting from Gly2 instead of Gly, we studied radiation-induced chemical evolution in Gly2 solid phase by irradiating it with 146 nm vacuum ultraviolet light of which photon energy was 8.5 eV.

Thin films of Gly2 were prepared with the vacuum evaporation technique which is reported elsewhere (Kaneko et al., 2005). In order to avoid thermal decomposition, the heating temperature was kept at around 360 K, which yielded the deposition rate of about $0.05\,\mathrm{nm\,s^{-1}}$. The thickness of the film was determined to be 300 nm from the optical linear absorption coefficient $\mu = 3 \times 10^5\,\mathrm{cm^{-1}}$ at wavelength 146 nm, by which thickness 99.99% of irradiated photons should be absorbed inside of the film. Thin films were irradiated with 146 nm vacuum ultraviolet light beam produced from Kr_2 excimer lamp with light intensity 6.9×10^{15} ($\mathrm{photons\,s^{-1}\,cm^{-2}}$) at the sample position. After the irradiation of VUV light beams, the irradiated sample was dissolved repeatedly in water drops of 10 μL with a pipette, and finally 50 μL of water solution was prepared. Chemical species in this water solution were analyzed by high performance liquid chromatography (HPLC). The sample before irradiation was also analyzed with the same procedure.

Fig. 1 shows typical data of the obtained chromatogram. The thin and the bold solid lines represent the chromatogram before and after the 120 s irradiation, respectively. In order to identify irradiation products, we studied chromatograms of pure reagents of diketopyperazine (dkp), Gly, Gly2, glycilglycilglycine (Gly3), and

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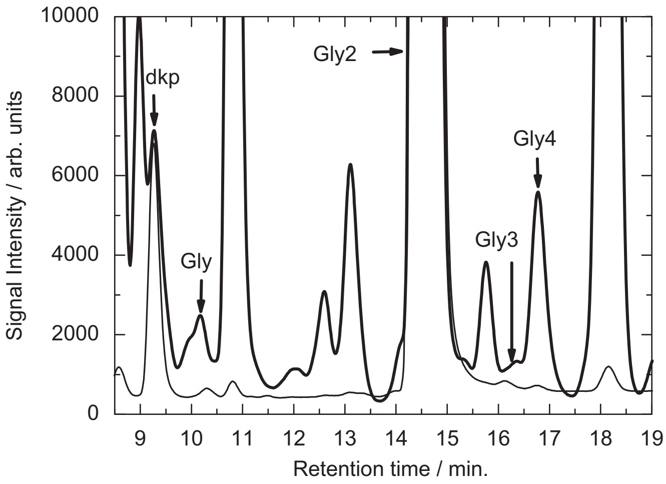

Fig. 1. HPLC chromatograms of glycilglycine films. Thin solid line curve: before irradiation with 146 nm vacuum ultraviolet light. Bold solid line curve: after irradiation.

glycilglycilglycilglycine (Gly4) as standard samples. We studied calibration curves of the concentration for these species and analyzed chromatograms of non-irradiated and irradiated samples. As seen from the figure, dkp was found in the non-irradiated film. Because dkp molecules were not found in the original Gly2 powder before evaporation, we concluded that dkp molecules were produced by heating during evaporation. Moreover, from the HPLC chromatograms after irradiation, production of Gly, Gly3, and Gly4 was also confirmed. The production of Gly and Gly3 was found to be smaller than that of Gly4. In Fig. 1, there are unidentified peaks at the retention times of 9.1, 9.9, 12.0, 12.6, 13.1, 14.1, 15.4, and 15.9 min. It is of interest to study the contribution of these species to the formation of dkp, Gly, Gly3, and Gly4. However, in this work, we concentrated our interest only on the formation rate of dkp, Gly, Gly3, and Gly4. In our separate study (Tanaka et al., 2008), according to mass spectrometry, we reported that deamination and decarboxylation reactions were the major chemical reactions. Studies on reaction pass though which dkp, Gly, Gly3, and Gly4 molecules are produced will be planned.

Fig. 2(a) and (b) shows the number of Gly, Gly3, and Gly4 molecules as a function of numbers of absorbed photons. Numbers of Gly and Gly4 molecules linearly increased with the increase in numbers of absorbed photons. Thus, by the best fit line shape analysis as shown in the figure, we estimated the production quantum efficiency of Gly, $\phi_{\mathrm{Gly2}\to 1}$ and Gly4, $\phi_{\mathrm{Gly2}\to 4}$ to be $(2.4\pm 0.1)\times 10^{-2}$ and $(3.7\pm 0.2)\times 10^{-4}$ molecules/(absorbed photon), respectively. For the case of Gly3, numbers of produced molecules were found to scatter as shown in the figure. At least it is clear that production quantum efficiency of Gly3 $\phi_{\mathrm{Gly2}\to 3}$ is smaller than that of Gly4 $\phi_{\mathrm{Gly2}\to 4}$.

The value of the decomposition yield of Gly2, η_{Gly2}, was estimated from the decrease of Gly2 peak area with the increase of irradiation time to be $(8.8\pm 1.0)\times 10^{-2}$. It should be noted that 91.2% of Gly2 molecules survived after absorption of an 8.5 eV photon.

The value of $\phi_{\mathrm{Gly2}\to 3}$ was smaller than $\phi_{\mathrm{Gly2}\to 4}$. This is reasonable, because the reaction from Gly2 to Gly4 is a one step chemical reaction; $(\mathrm{Gly2}+h\nu)+\mathrm{Gly2}\to \mathrm{Gly2}^{*}+\mathrm{Gly2}\to \mathrm{Gly4}$, while that from Gly2 to Gly3 was thought to be of two step reaction; $(\mathrm{Gly2}+h\nu)+\mathrm{Gly2}\to \mathrm{Gly}+\mathrm{Gly}+\mathrm{Gly2}\to \mathrm{Gly}+\mathrm{Gly3}$. Here, $h\nu$ means the energy of incident VUV light and the mark * designates that the molecule is excited.

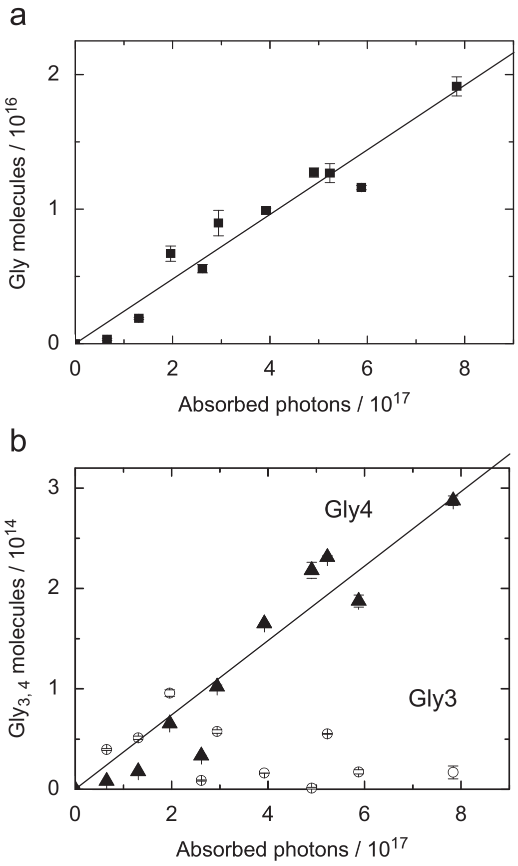

Fig. 2. (a) Numbers of produced Gly molecules as a function of numbers of absorbed 146 nm photons. (b) Numbers of produced Gly3 and Gly4 molecules as a function of numbers of absorbed 146 nm photons.

3. Soft X-ray natural circular dichroism (SXNCD) of solid amino acids

Cronin and Pizzarello (1997) reported that the enantiomeric excess was found in amino acids in some meteorites. The contribution of the circularly polarized ultraviolet radiation has been discussed with the possibility to induce the asymmetric reaction (Bailey et al., 1998). Since soft X-rays are known to be strongly interactive with matter and are thought to be the energy source of chemical evolution in space, it is of interest to study the asymmetric reaction induced by the irradiation of circularly polarized soft X-rays to amino acids. In the first experimental result (Tanaka et al., 2005), energy resolution was not so good enough to resolve the $1s\to\pi^{*}$ transitions at around 532 eV of two oxygen atoms of the COO^{-} part of amino acids. Thus, we have tried the detailed measurement of SXNCD spectra, especially tried to resolve the $1s\to\pi^{*}$ transitions. Here we report our new results of SXNCD spectra of amino acids with the focus at the $1s\to\pi^{*}$ transitions.

Thin films of D- and L-serine, and D- and L-alanine were prepared with the vacuum evaporation technique on SiN membrane. The thickness of films was adjusted to be about 300 nm to yield the 10% transmittance of the 540 eV photons. Measurements were carried out at the beamline BL25SU of the SPring-8, Japan. Right- and left-circularly polarized soft X-ray beams produced from the twin-herical undulators were used for polarization modulation spectrometry (Muro et al., 2005). The frequency of polarization switching was set at 1 Hz. Because the soft X-rays emitted from the undulator were quasi-monochro-