



keV ion irradiation of solid glycine: an EPR study

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Abstract

The radicals formed in keV ion irradiation of solid glycine were studied using electron parameter resonance (EPR). Spectra were observed at different temperature from 100 to 310 K after irradiation at room temperature. Different radicals are formed in different radiation conditions. The structure and concentration of the main radicals formed under 30 keV ion irradiation remain stable in different measurement temperature and radicals formed under 20 keV ion irradiation vary. The results indicate that more kinds of radicals are formed under keV ion irradiation which is attribute to the nuclear collision process. It is in agreement with previous study with mass spectrometer. © 1998 Published by Elsevier Science B.V.

1. Introduction

In recent years there has been growing interest in keV ion bombardment of organic materials [1–7]. The interest for practical applications, is due to the potential of keV ion beam such as SIMS [7–11], FAB [11,12] and surface modification [13–15]. Our interest is its biological effects and application in breeding of plants and microbes [16,17]. keV ion irradiation often causes different biological and chemical effects than other radiation [18–20]. The mechanism of the effects is still ambiguous. Studies on the behavior of intermediates, such as radicals or ions, in organic solids are necessary to elucidate the mechanism of the effects. Electron

parameter resonance (EPR) was widely used to study the organic radicals produced by radiation as well as other methods, and also used to study the organic radicals induced by keV ion irradiation of polyaniline [15], seeds [21] and DNA [22]. Amino acids are the basic components of proteins and glycine is the simplest amino acid. In this paper, we concentrate on the chemical structures of free radicals formed under the irradiation of keV ions on glycine and their changes in different conditions.

2. Experiment and methods

The glycine used was commercially available and was recrystallized before use. It was dissolved with distilled water, placed onto a glass plate and was dried to become a thin layer. The thinness of

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the sample is about 2 μm . The N ion beam was produced by the first ion beam breeding machine in China. The sample of thin layer glycine was irradiated by nitrogen, its energy was chosen from 2.0 to 30 keV, its pulse in current was 30 mA, pulse time is 0.5 s, and interval is 55 s. The temperature is controlled below 50°C. Fluence of each pulse to the same sample was about 10^{14} ions/cm².

EPR spectra were taken on a Bruker ER-200D-SRC at X-band (9.7 GHz) 15 h after glycine was irradiated at room temperature by keV nitrogen ion. Data were acquired and evaluated by an IBM-PC compatible 386 computer EPR data system which was designed by Xiamen University of China. DPPH was used as reference to obtain the g value of radicals.

3. Results

Polycrystalline glycine, irradiated with 30 keV nitrogen ions at dose of 70 pulses in room temperature, give EPR spectrum at different temperatures as shown in Fig. 1. The main peak was normalized to the same height. At 100 K, there is only a single peak in the spectrum and the single peak is the

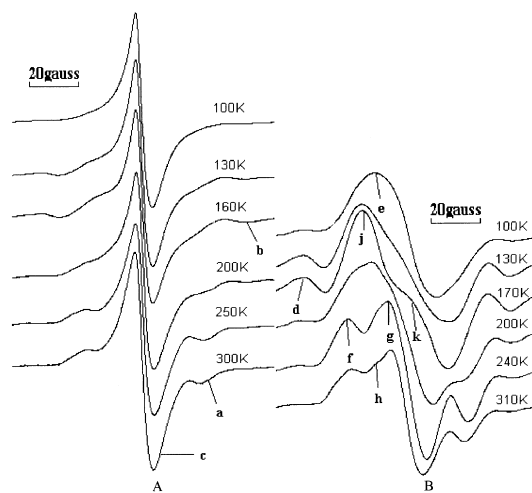


Fig. 1. The qualitative EPR spectra of glycine irradiated by nitrogen ion at room temperature. The measurements were carried out at different temperature. The spectra were recorded after the sample was kept at room temperature for about 15 h: A. 30 keV, 70 pulses; B. 20 keV, 10 pulses.

main part of EPR spectra of glycine at different temperatures. They are rather different from previous work which show a spectrum consisting of two broad lines separated by about 28 G in the irradiation of glycine at 77 K [23] or a triplet with separation of 41 G at room temperature [24,25]. At 130 K, two new peaks (b) can be obviously observed and two peaks (a) exist near the main peak. At 250 K, peaks (a) become rather large to be clear for observation and overwhelm the peaks (b). It can be seen from Figs. 2(A) and 1(A) that the peak (c) decreases and peak (a) increases when the temperature increases and the peak (b) reaches maximum at about 160 K. The p-p width value of main peak in different temperatures is all about 7 G. The split width of peaks (a) from main peak is about 21 G and peaks (b) from main peak is about 41 G. As the strength of peak (a) and (b) varies with different trends at different temperature, they are not produced simply by a quintuplet. The peak (a) is attributed to $\bullet\text{CH}_2\text{COOH}$ (a) for the split of the peak (a) is about 40 G [23]. The separation of peak (b) is about 82 G, we can attribute it to $\bullet\text{CH}(\text{NH}_3^+)\text{COO}^-$ (b) whose EPR spectrum is a 1:3:4:4:3:1 sextet [24]. Although the sextet cannot be seen in our EPR spectrum, a strong single peak may overwhelm the sextet. The main peak is too strong to be explained as a part of triplet or other multiplet. There are more than three kinds of radicals in the glycine after irradiated with 30 keV nitrogen ion based on above analysis. The main radicals (c) is a single peak, the g -value of the main peak is 2.0023, so it may be trapped electron.

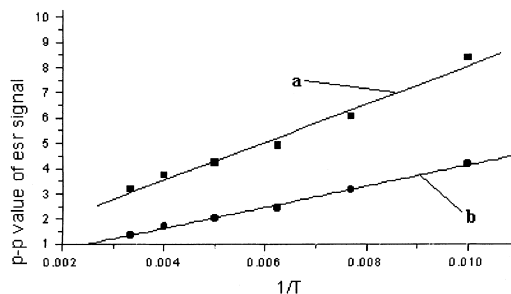


Fig. 2. Radical concentration in irradiated glycine via $1/T$: (a) the glycine was irradiated by 30 keV N ion with dose of 30 pulses; (b) the glycine was irradiated by 30 keV N ion with dose of 10 pulses.

Through simulation, a doublet may exist in the spectra. As the peak strength is rather weak, the isotopic split of ^{13}C is not obtained in all spectrum. As the glycine is irradiated at room temperature, the change of radicals is a reversible process.

In most case in our experiments, the EPR spectrum of glycine irradiated by keV nitrogen ion is similar to the patterns in Fig. 1(A), especially when the energy is 30 keV. The main peak strength also decreases with the increment of EPR measurement temperature. Fig. 2 is the p–p height of the main EPR peak at different temperature when the glycine samples were irradiated at the energy of 30 keV with dose of 30 pulses and 30 keV with dose of 10 pulses. We use linear formula to simulate the correlation between radical concentration and $1/T$ as shown in Fig. 2 which indicates that the signal strength of radical is inversely proportional to temperature. It indicates that radical concentration in solid glycine is stable at different temperatures according to Curie's law and can be inferred that the same main radicals were produced in these irradiation condition.

When the ion energy is less than 25 keV and dose is less than 10 pulses, the types of radicals are different. Fig. 1(B) is the EPR spectrum of glycine irradiated by 20 keV N ions with a dose of 10 pulses measured at different temperatures. It is obvious that there are more kinds of radicals in the sample. At different temperatures, the strength and p–p width of the main EPR signal have complicate variances as shown in Fig. 3. Fig. 3(a) shows the p–p width value of different temperatures, it shows that the main radicals in the sample vary in different temperatures. As the p–p width

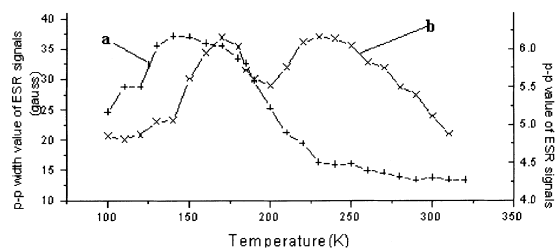


Fig. 3. Variance of main peak in Fig. 1(B) in different temperature: (a) the p–p width value of the main peak in Fig. 1(B); (b) the p–p value of the main peak in Fig. 1(B).

value increases from 25 to 37 G and decreases from 37 to 13 G, the main radicals in different temperature are all different from the main radical formed by higher energy ion bombardment. In Fig. 1(B), as the split width of peaks d and f from main peaks are 43 and 22 G, respectively, the radical b and a exist in the glycine sample irradiated at 20 keV with dose of 10 pulses. From the EPR spectra of 130 and 170 K in Fig. 1(B)(k), it can be inferred that radical c was also produced at 20 keV with dose of 10 pulses. It is difficult to explain the complicated main peak from the present data because of the poor resolving power of our experiment, however we try to give some explanations, there are probably three other radicals shown as peak j at 170 K, g at 240 K and h at 310 K. The peak e at 100 K is the sum of j, h and k, the main peak at 200 K is the sum of j and h. When the temperature increased from 100 to 170 K, the radical in peak k decreased rapidly, and peak h decreased slowly. When the temperature increased from 170 K, the peaks f and g increased. From the EPR spectrum at 200 K (h), the p–p width of main peak is about 29 G and we can attribute it to $\text{NH}_2\text{CH}_2\text{COOH}^-$ [23] whose EPR spectrum is two broad lines separated by about 28 G.

The variance of radical concentration at different doses is shown in Fig. 4 when the glycine was irradiated by 30 keV nitrogen ion at room temperature. It is shown that the radical concentration increased when the dose increased at lower dose, it reached maximum when the dose increased to 20 pulses, and decreased slowly with the increasing



Fig. 4. The variance of radical concentration in irradiated glycine at different dose the sample was irradiated with 30 keV nitrogen ion at room temperature and the EPR spectra were recorded at room temperature after the sample was kept at room temperature for about 15 h.

of dose. This observation is similar to γ -rays, MeV protons and helium ions [25,26]. When the sample was irradiated with 20 keV ions, it gave a similar pattern as when the radical concentration reached maximum at higher dose. Previously, Slifkin et al. pointed out that this kind of dose-effects curve is the evidence that there are two different kinds of trapping sites, ones which can be re-used many times and others which can be used once in irradiation of amino acids. It shows that the two kinds of trapping sites are formed in the keV ion irradiation.

After the glycine was irradiated with 20 keV nitrogen ions with a dose of 10 pulses, we measured the EPR spectrum at different times to obtain the variance of the radical concentration with stored time as shown in Fig. 5. It can be seen that the radical concentration of the sample decreased initially and remained stable later which fit the exponential decreasing. However, the EPR spectrum remained the same when the sample was stored for a long time.

When the glycine was irradiated with different energy nitrogen ion, the EPR spectrum is different as shown in Fig. 6. The main difference is the variance of the strength of the secondary peaks. The types of radicals also varied at different energy ion irradiation: the p-p width at 30 keV ion irradiation is rather smaller than those at lower energy ion irradiation. It is more likely that more than one kind of radicals form the main EPR peak in Fig. 7 at 25 and 17.5 keV. The peak at about 3515 G in the Fig. 7 is the signal of Mn^{2+} which may be from the glass for the signal only can be seen when a little sample deposited on the plate of glass for irradiation.

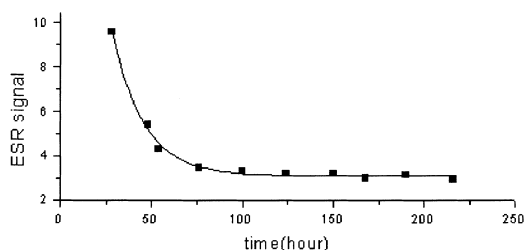


Fig. 5. Variance of the radical concentration in ion irradiated glycine with stored time.

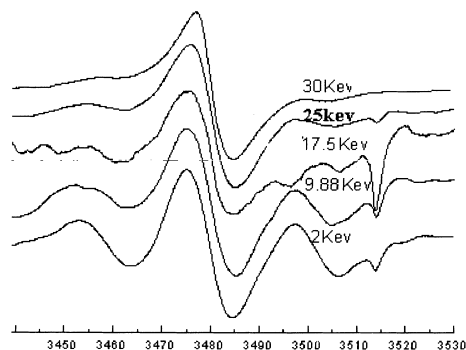


Fig. 6. The EPR spectra of glycine irradiated by nitrogen ion with different energy at room temperature. The dose is 20 pulses. The spectra were recorded after the sample was kept at room temperature for about 15 h.

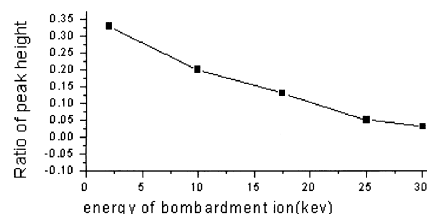


Fig. 7. The ratio of peak height at different energy irradiation.

The ratio of height between the secondary and main peak was calculated and shown as Fig. 7 at the different energy ion irradiation. The radical in secondary peak should be $\bullet CH_2COOH$ (b). The result shows that $\bullet CH_2COOH$ in glycine decreases to nearly zero at room temperature when irradiation energy increases from 2 to 30 keV.

4. Discussion

The basic chemical structure of most of the radicals formed by irradiation of glycine is known from previous studies using single crystals [23,24] or the spin trapping methods [27–29]. $\bullet CH_2COOH$ and $\bullet CH(NH_3^+)COO^-$ have been positively identified following irradiation at 300 K as the main radicals of glycine [23]. However, different spectra are observed if the irradiation and examination are carried out at 77 K [30]. Furthermore, if the sample is irradiated at 77 K and warmed slowly to 300 K only one species $NH_2CH_2'COOH^-$ is observed

[24,31]. In keV ion irradiation of glycine, although $\bullet\text{CH}_2\text{COOH}$ and $\bullet\text{CH}(\text{NH}_3^+)\text{COO}^-$ are observed at different conditions including different temperatures of examination, radiation dose and energy of ion, the main radicals vary and often cannot be determined in the present study. An important fact has been established by these experiments. The types of radicals produced in solid glycine by keV ion irradiation seem to be more than other types of irradiation. When the energy of bombardment ion is lower than 10 keV, $\bullet\text{CH}_2\text{COOH}$ is the main radical. When the energy of bombardment ion is more than 30 keV, the trapped electron may be the main radical. When the energy of bombardment of ion is between 10 and 30 keV, the main radical may include several radicals and vary at different temperatures. It seems that the energy of bombardment ion influences the formation of radicals in the keV ion irradiation. We attribute the influence to the nuclear collision process between the implanted ion and sample molecule.

Previously, we pointed out that the energy loss through nuclear collision process is one of the main processes contributing to the radiation effects and first correlated the nuclear collision process with the breeding mechanism of keV ion irradiation [20]. Online mass spectrometer analysis in 8 keV Ar atom bombardment indicates that keV ion or atom bombardment forms more kinds of intermediates in the study of threonine and glycine [32]. They are the direct evidence to the above view. In the EPR study of keV ion irradiation of glycine, more kinds of radicals are formed in agreement with previous results of on-line mass spectrometer. The difference of EPR spectra between 30 and 20 keV ion irradiation may be explained with the same view. When the energy of incident ion is about 15 keV, the nuclear energy loss is equal to the electronic energy loss. When the energy of ion increases from 15 keV, the electronic energy loss increases and nuclear energy loss decreases.

This work is an initial study of radicals formed in the keV ion irradiation of glycine. Many kinds of radicals are formed in the keV ion irradiation, although the chemical structure of some radicals have been elucidated in a previous work, there are still a lot of radicals which have not been deter-

mined in this work. Further experiments should more selectively focus on these radicals leading to a better understanding to the process of keV ion irradiation.

Acknowledgements

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