

CRYSTAL LATTICE DEPENDENCY OF THE FREE RADICALS FOUND IN IRRADIATED GLYCINE *

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The EPR spectra, and hence the stable free radicals, are different for the X- or γ -irradiated α -, β - and γ -crystal forms of polycrystalline glycine. Therefore comparisons of the trideutero-glycine EPR spectrum with the EPR spectra of non-deuterated glycine are open to question.

In the course of our studies on the radiolysis of glycine, we compared the EPR spectra obtained after irradiation of different crystal forms of normal glycine and trideutero-glycine ($\text{ND}_3^+\text{CH}_2\text{CO}_2^-$). Glycine may exist in three crystal modifications: the α -form, which is formed by crystallizing glycine from an aqueous solution; the β -form, which crystallizes upon adding ethanol to a hot saturated aqueous glycine solution [1] and the γ -form, which crystallizes from a hot saturated solution of glycine in aqueous acetic acid [2]. The crystal structures of all these modifications are known [3-5].

We also studied glycine prepared by freeze drying a 10% aqueous glycine solution and furthermore trideutero-glycine, obtained by recrystallizing glycine three times from a heavy water solution.

EPR spectra of the powdered glycine samples, exposed at 283°K in a 10 Torr nitrogen atmosphere or in vacuum to X- or γ -irradiation (exposure dose between 0.05 and 5 Mrad) were obtained with an X-band EPR spectrometer equipped with 100 kc modulation, modified Pound stabilization and a double cavity (TE104) [6].

The EPR spectra we obtained after an exposure dose of about 0.2 Mrad are shown in fig. 1. The spectra of irradiated α -, β - and freeze-dried glycine are almost identical. This suggests that the radicals in these forms of glycine

are practically the same. The small differences in the spectra for α - and freeze-dried glycine (which has the α -glycine structure) could be due to the different crystal sizes. The crystal structure of β -glycine is almost the same as for α -glycine and in addition β -glycine changes so easily into α -glycine (upon mechanical shock or at 100°C) that the radiation could also have effected the change.

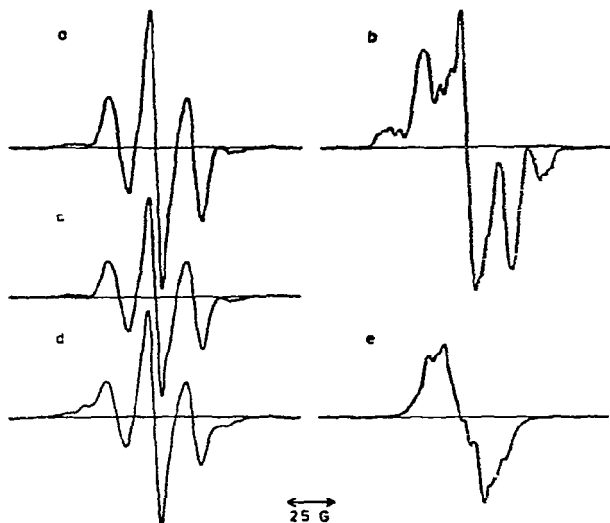


Fig. 1. Derivative EPR spectra of X-irradiated (0.2 Mrad at 283°K, measured at room temperature) polycrystalline powders of α -glycine (a), γ -glycine (b), β -glycine (c), freeze-dried glycine (d) and glycine- d_3 (e). The static magnetic field increases from left to right.

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The EPR spectrum of γ -glycine is quite different from the other non-deuterated glycine spectra. In fact, it seems that in γ -glycine only *one* radical is present, namely $^1\text{NH}_3\dot{\text{C}}\text{HCO}_2^-$, whereas in α -, β - and freeze-dried glycine both the radicals $\dot{\text{C}}\text{H}_2\text{CO}_2^-$ and $^1\text{NH}_3\dot{\text{C}}\text{HCO}_2^-$, reported by Morton [7] and other authors, are present.

The EPR spectrum of trideuteroglycine could now arise from either only the $^1\text{ND}_3\dot{\text{C}}\text{HCO}_2^-$ radical, as in γ -glycine, or from both $\dot{\text{C}}\text{H}_2\text{CO}_2^-$ and $^1\text{ND}_3\dot{\text{C}}\text{HCO}_2^-$, as in the other glycines. The overall width and shape of the spectrum, a re-evaluation of the reported results of Weiner and Koski [8] and chemical evidence [9] suggest that the EPR spectrum of trideuteroglycine is caused by the radical $^1\text{ND}_3\dot{\text{C}}\text{HCO}_2^-$ only. This is interesting because Iitaka [4] has suggested that trideuteroglycine could have the γ -glycine crystal structure.

The above results indicate that radical formation in a substance can be dependent on the crystal structure. Hence one has to be quite certain that the crystal structure of a deuterated compound is the same as that of the non-deuterated one, before one attempts to analyze the EPR spectrum on the basis of comparisons between the spectra of unlabelled and deuterium labelled compounds. In fact, the best way of labelling of compounds in order to facilitate the interpretation of EPR spectra would be the substitution of a heavy atom, for instance ^{13}C or ^{15}N for ^{12}C or ^{14}N respectively, because the substitution of ^2D for ^1H is accompanied by a profound isotope effect and often causes crystal lattice expansion [10].

The large number of radicals, proposed by numerous authors to explain the features of the glycine EPR spectra, were mostly due to comparisons between the spectra of unlabelled and deuterium labelled glycines. This study indicates that such assignments must be considered

with caution. In fact, the complete radiolysis of glycine can be explained on the basis of only three radicals, namely e^- or $^{\bullet}\text{H}$, $^{\bullet}\text{CH}_2\text{CO}_2^-$ and $^1\text{NH}_3\dot{\text{C}}\text{HCO}_2^-$, or their ionic precursors [11], formed during radiolysis. Of these, only the two large radicals have been observed and identified at the end of the radiolysis [7]. It is not necessary to assume selective hydrogen transfer processes, as suggested by Morton, to explain the erroneous interpretations of, for instance, Weiner and Koski [8] and earlier authors.

We found also that the crystal structure does not affect the dose dependency of the total free radical concentration. The same dose leads in all modifications to the same concentration, although the relative proportions of $^{\bullet}\text{CH}_2\text{CO}_2^-$ and $^1\text{NH}_3\dot{\text{C}}\text{HCO}_2^-$ differ. The G_0 value we found is about 3.2 [9]. We assume therefore that the primary processes during the radiolysis do not depend on the crystal form. The secondary processes, such as radical abstraction reactions etc., however, appear to be quite sensitive to changes in crystal modification.

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