

FT EPR STUDY OF PHOTO-OXIDATION PROCESSES AT BUILDING UNITS OF PROTEINS AND THEIR DERIVATIVES

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Using time-resolved Fourier transform electron paramagnetic resonance (FT EPR) spectroscopy the photo-oxidation of glycine (Gly), alanine (Ala), glycine esters (GlyOR) and N,N-dimethylglycine (DiMeGly) and N,N-dimethylglycine ethyl ester (DiMeGlyOEt) by spin-polarized triplets of anthraquinone-2,6-disulfonate was studied in aqueous solution in the pH range 6...10. The quinone radical anion shows an emissive spin-polarization (CIDEP) indicating an electron transfer reaction from the investigated molecules to the spin-polarized quinone triplet. Using glycine as an electron donor the radical species $^+\text{NH}_3/\text{NH}_2-\dot{\text{C}}\text{H}_2$ were identified as transient products formed on the nanosecond time scale over the whole pH range. The radicals have been found to originate from two different reaction channels depending on the pH. The kinetics of both reaction channels is studied by optical transient spectroscopy and time resolved FT EPR spectroscopy.

In an irradiated system with electron donor GlyOMe or GlyOEt the aminyl radical $^+\text{NHCH}_2\text{COOR}$ and the glycylic-type radical $\text{NH}_2\dot{\text{C}}\text{HCOOR}$ (R represents for $-\text{CH}_3$ or $-\text{CH}_2\text{CH}_3$) formed by fast deprotonation of the glycine ester radical cation, have been detected. In addition, two isomeric forms (E and Z) of the glycylic-type radical $\text{NH}_2\dot{\text{C}}\text{HCOOR}$ were unambiguously identified. The assignment to the two isomers was supported by quantum chemical DFT calculations. With N,N-Dimethylglycine esters as electron donor the ammonium radical cation was detected as the primary oxidation product decaying into the radicals $\text{C}-\text{H}_2\text{N}(\text{CH}_3)-\dot{\text{C}}\text{H}_2-\text{COOEt}$ and $\text{C}-\text{H}_2-\dot{\text{C}}\text{OEt}$, respectively.

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