

# PHOTO-OXIDATION OF METHIONINE AND ITS DERIVATIVES STUDIED BY TIME-RESOLVED CIDNP [IL-04]

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Time-resolved chemically induced dynamic nuclear polarization (tr-CIDNP) method combining site-specificity of EPR and NMR with high sensitivity allows structural characterization and determination of reaction kinetics of complex photoreactions in biological system. The present work describes the results of a comprehensive CIDNP study of the reactions of methionine, 3-methyl-thiopropylamine and dipeptide Met-Gly with 4-carboxy-benzophenone and 9,10-antraquinone-2-sulfonate sodium salt in aqueous solution at different pH (6.7-13.3). At pH values above  $pK_a$  of the amino group, the radical cation exists in a cyclic form with a two-center three-electron bond between the nitrogen and sulfur atoms, whilst in solutions when amino group is positively charged, the radical cations have linear structure.<sup>1</sup> The kinetics of the polarization of 3-(methylthio)propylamine and Met-Gly peptide demonstrated that the cyclic radical does not undergo deprotonation with the formation of a linear amino radical, as it was assumed earlier from ESR experiments. Instead, the deprotonation of charged amino group of Met-Gly occurring on microsecond time scale was detected that leads to formation of cyclic radical of Met residue. The comparison of the experimental results with literature data obtained by steady state CIDNP measurements for Met casts doubt on the hypothesis that interconversion between three types of methionine cation radicals occurs.

The competitive channel for oxidative quenching of the triplet sensitizer by direct electron transfer from the nitrogen atom leading to formation of the aminium radical cation was revealed in strongly basic solution as a common feature of other amino acids. The photooxidation pathways for methionine and the dipeptides Met-Gly and Gly-Met depend on pH. As pH increases above 11, the efficiency of electron transfer from the amino group with the formation of the aminium cation radical becomes higher.

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[1] Morozova, O. B.; Korchak, S. E.; Sagdeev, R. Z.; Yurkovskaya, A. V., *J. Phys. Chem. A* 2005, 109, 10459-10466.