

## A CIDNP study of the reduction of short-lived thymine radicals by aromatic amino acids

Fishman Natalya N.,<sup>1\*</sup> Morozova Olga B.,<sup>1</sup> Vieth Hans-Martin,<sup>1,2</sup>  
Yurkovskaya Alexandra V.<sup>1</sup>

<sup>1</sup> International Tomography Center, Institutskaya 3a, 630090 Novosibirsk, Russia

<sup>2</sup> Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

\* E-mail: [n\\_s@tomo.nsc.ru](mailto:n_s@tomo.nsc.ru)

As a model for chemical DNA repair, the reduction of thymine radicals in their reaction with aromatic amino acids has been studied by time-resolved chemically induced dynamic nuclear polarization (CIDNP) technique. To generate the thymine radicals in a wide pH range in aqueous solution pulsed laser irradiation was implemented to a solution containing the photosensitizer 3,3',4,4'-tetracarboxy benzophenone (TCBP), thymine, and amino acid (tryptophan, N-acetyl tryptophan, tyrosine or histidine). As a preliminary step, the photoinduced oxidation of thymine by triplet-excited 3,3',4,4'-tetracarboxy benzophenone was studied and thymine radical intermediates were characterized by means of CIDNP. It was shown that proton-coupled electron transfer (PCET) from neutral thymine to the triplet excited photosensitizer in neutral aqueous solution (pH 6.3) leads to the formation of a neutral thymine radical; its formation is preceded by the formation of an elusive cationic thymine radical on the geminate stage of the reaction. In contrast, in basic solution (pH 11.7) a thymine anion reacts with the triplet excited photosensitizer by electron transfer resulting in the formation of a TCBP radical anion and a neutral thymine radical. The latter deprotonates rapidly, and a thymine radical anion is formed at these conditions. The complementary measured magnetic field dependences of CIDNP has confirmed reaction mechanism. The reduction of the neutral thymine radical at pH 6.3 and to the thymine radical anion at pH 11.7 by tryptophan was revealed by comparing CIDNP kinetic data in the photoreactions of triplet TCBP and thymine with the respective data obtained for triplet TCBP and thymine and tryptophan (or N-acetyl tryptophan). The rate constants for the reduction of neutral and anionic thymine radicals by tryptophan and N-acetyl tryptophan were determined from quantitative analysis of the CIDNP kinetics, which is sensitive to the rates of fast radical reactions. We also have qualitatively investigated the kinetics of the reduction of thymine radicals by tyrosine or histidine in a wide pH range in aqueous solution since it turned out that this reaction gives a large amount of by-products in the presence of tyrosine or histidine.

The experimental part of this work was supported by Russian Science Foundation (project no. 20-63-46034) and the theoretical modelling was supported by the Ministry of Science and Higher Education of the Russian Federation (Grant No. 075-15-2021-580).