

New Insights into the Reaction Path of 4-Carboxybenzophenone Triplet with Oligopeptides containing N- and C-terminal Methionine Residues

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Methionine is one of the easiest amino acid residues in proteins to oxidize. If the oxidation is completed to the sulfoxide, this can be repaired in a biological environment. But if the oxidation can be stabilized at the one-electron oxidation level, this can lead to deleterious biological results. Neighboring groups can stabilize the sulfur radical cation, and this has been studied in some detail. In the current work, we address the dynamics of the flexible side group of an oxidized methionine. As a probe for this intramolecular dynamics along a polyproline bridge, Met-(Pro)_n-Met, we followed the formation of dimeric S-S radical cations subsequent to the photosensitized formation of monomeric S radical cations in either the C- or N-terminal methionines. The observed yields were related to the underlying reaction rates via Langevin dynamics computations of the probability distributions of S-to-S distances that, in turn, could be used to obtain diffusive dynamics by a statistical-mechanical theory of Szabo, Schulten, and Schulten. From the analysis, it was found that in the shorter proline bridges, the formation of S-S dimeric radical cations were found to be activation limited, but diffusion limited in the longer proline bridges. The Met-(Pro)_n-Met in this work were at a pH (5.7), where the peptides were zwitterions. They showed a faster diffusion rate along the polyproline chains that did these same protonated peptides from our earlier study at pH 1 (the peptides in the cationic forms).

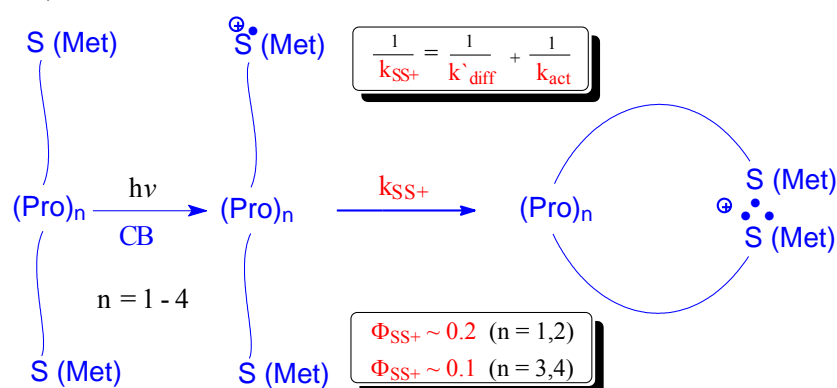


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