

## Intramolecular Dissociative Electron Transfer Through Peptide Bridges

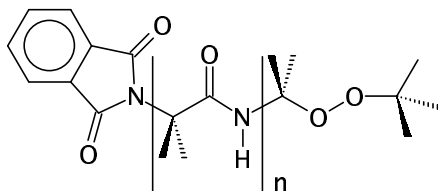
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The study of intramolecular electron transfer (ET) reactions in Donor-Spacer-Acceptor (D-Sp-A) molecular systems has proved to be a very powerful approach to understand the mechanism by which electrons are transferred through bonds and space. From this point of view, however, much less is known for dissociative ETs. In these processes, for which the relevant theory has been proposed and developed by Savéant during the last 15 years,<sup>1</sup> ET and cleavage of a sigma bond are concerted. Recently, we investigated some intramolecular dissociative ETs in systems in which the spacer was cyclohexyl or just a single methylene unit. Much of the focus was on the free energy dependence of the intramolecular dissociative ET rate<sup>2</sup> and the problem of understanding the nonadiabatic character of these processes.<sup>3</sup> We are now investigating the role played by biologically relevant bridges. More specifically, we started studying the distance dependence of the dissociative ET rate in systems in which the bridges are synthetic peptides based on the  $\alpha$ -aminoisobutyric acid residue (Aib). These peptides are particularly interesting because of the remarkable stability and rigidity of their secondary structure ( $3_{10}$ -helix).<sup>4</sup>

In the present communication, we analyze the distance dependence of the intramolecular dissociative ET rate in purposely-synthesized D-Sp-A systems having the following general structure (n is the number of Aib units):



The phthalimide moiety, which is easily reduced to its radical anion, was selected as the donor. The peroxide functional moiety, a well-defined dissociative-type acceptor,<sup>5</sup> completed the D-Sp-A system. Main goal of our investigation was to understand the role of the poly-Aib backbone and the relevance of intramolecular hydrogen bonds in mediating the electron transfer process.

The redox properties of models of both D and A were analyzed and the intermolecular ET rate was determined by homogeneous redox catalysis. The intramolecular ET rate in the D-Sp-A systems, in which n was varied from 1 to 7, was obtained by analysis and simulation of the cyclic voltammograms. The distance dependence of the intramolecular ET rate constant will be analyzed in comparison with complementary information aimed at monitoring the dependence of the secondary structure formation on the number of Aib units.

## References

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