Anomalous Distance Dependence of Electron Transfer across Aib Oligo-Peptide Bridges

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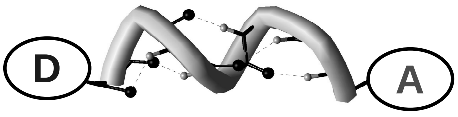
The peptide backbone is essential in assisting long-range electron transfer (ET) in proteins.[1] To understand how the electron tunneling between a donor (D) and an acceptor (A) takes place, it is thus necessary to take into account the chemical structure and conformational characteristics of the peptide bridges. Most of the results obtained with model peptides concern the ET across oligoproline bridges.[2,3] Some of these results have been attributed to a transition between the superexchange and the sequential hopping mechanisms.[2,4] On the other hand, hydrogen bonding has been recognized to affect the electronic coupling and thus the ET rate between D/A couples.[5] This is a feature of which oligoprolines are obviously lacking. To investigate systematically how distance increase and concomitant intramolecular H-bond formation impact the electron tunneling, we devised a series of structurally well-defined peptide systems. We report and discuss here the results obtained on the electrochemically-induced dissociative ET[6] between donors and peroxide acceptors connected by oligopeptide spacers (Sp), as illustrated in the model below.



The peptides of choice were based on the α-aminoisobutyric acid (Aib) residue. Aib oligomers are well known for their propensity to form rigid 3_{10}-helices because of steric hindrance at the α-carbon and the resulting restricted torsional freedom.[7] The experimental methodologies were as described for other D-Sp-A systems.[8] The key motif of the peptide systems investigated is that an increase of the number of Aib units does not solely result in a larger D/A separation but it is also accompanied by concomitant increase of the number of H-bonds and, consequently, by a remarkable increase of the stiffness of the peptide backbone. Our study revealed that not only intramolecular H-bonds are important but also that they may even contrast efficiently an increase of the separation between D and A. We are currently working to verify whether or not these conclusions hold when the energetics of the D, Sp, and A components are altered significantly.

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