

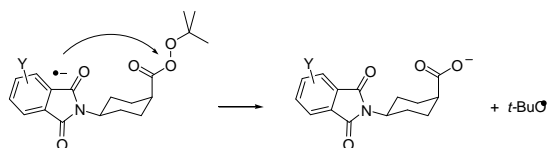
Driving-Force Dependence of Intramolecular Dissociative Electron Transfers

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Predicting the rate of chemical reactions as a function of driving force and environmental parameters is a challenging and stimulating task. In this connection, the most important achievements have been probably reached in the area of electron-transfer processes, thanks to the Marcus theory of outer-sphere electron transfer and its subsequent implementations.^{1,2} In recent years several groups have collected data and provided relevant insights into the dynamics of intermolecular dissociative electron transfers, as recently reviewed.^{3,4} On the other hand, less information is available on the corresponding intramolecular processes.^{5,6} To study the relationship between rate and driving force of intramolecular dissociative electron transfers, a series of donor-spacer-acceptor (D-Sp-A) systems has been devised and synthesized. *cis*-1,4-Cyclohexanediyl and a perester functional group were kept constant as the spacer and acceptor, respectively. By changing the aryl substituents of the phthalimide moiety, which served as the donor, the driving force could be varied by 0.74 eV. X-ray diffraction crystallography and *ab initio* conformational calculations pointed to D-Sp-A molecules having the *cis*(cyclohexane) equatorial(phthalimido)-axial(perester) conformation and the same D/A orientation. The intramolecular dissociative electron-transfer process was studied by electrochemical means in DMF, in comparison with thermodynamic and kinetic information obtained with models of the acceptor and the donor. The intramolecular process consists of the electron transfer from the electrochemically generated phthalimide-moiety radical anion to the peroxide functional group.



The electrochemical analysis provided clear evidence of a concerted dissociative electron transfer mechanism, leading to the cleavage of the O-O bond. Support for this mechanism was obtained by *ab initio* MO calculations, which provided information about the LUMO of the acceptor and the SOMO of the donor. The intramolecular rate constants were determined and compared with the corresponding intermolecular values, the latter data being obtained using the model molecules. As long as the effective location of the centroid of the donor SOMO does not vary significantly by changing the aryl substituent/s, the intramolecular dissociative electron transfer obeys the same main rules already highlighted for the corresponding intermolecular process. On the other hand, introduction of a nitro group drags the SOMO away from the acceptor and, consequently, the intramolecular rate constant is smaller than the expected value. Therefore, a larger solvent reorganization than for intermolecular electron

transfers and the effective D/A distance and thus electronic coupling must be taken into account for quantitative predictions of intramolecular rates.

References

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