

ELECTROSTATIC CATALYSIS OF NON-REDOX REACTIONS

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It is well known that the rate of redox reactions can be manipulated by means of an electrical potential gradient. However, in this talk we will show that electrostatic catalysis is also a practical possibility for manipulating non-redox processes. As elegantly demonstrated by Shaik and co-workers, many formally covalent species can be stabilized by resonance between their covalent and one or more charge-separated mesomeric forms.¹ In principle, if an electric field is oriented in such a way as to electrostatically stabilize one of these minor contributors, the amount of resonance will increase and the species will be stabilized accordingly. As an example, Shaik and co-workers showed via quantum-chemical modelling that an oriented electric field (OEF) could be used to promote selectivity between the exo and endo products of a simple Diels-Alder reaction, and also lower the activation barriers.^{1b} However, for electrostatic catalysis to be achieved in practice, the orientation of the reactants would have to be controlled. Together with collaborators, we have been using a combination of theory and experiment to explore two alternative solutions to this problem. The first is using surface chemistry techniques, in conjunction with the break-junction technique in scanning tunnelling microscopy, to probe unfavourable Diels-Alder chemical reactions (see Fig. 1).² This allows us to detect chemical reaction events at the single molecule level, whilst delivering an oriented electrical field-stimulus across the approaching reactants. In the second approach, we have instead addressed problem of orientation of the electric field by making use of appropriately placed charged functional groups to provide the electrostatic stabilization for solution-phase reactions.³ In this way, the direction of the local field experienced by the reaction centre is fixed, and by associating the stabilization or destabilization with the protonation state of an acid or base group, it has the advantage of providing a convenient pH switch. In this talk our experimental and theoretical results will be presented and the broader prospects for electrostatic catalysis discussed.

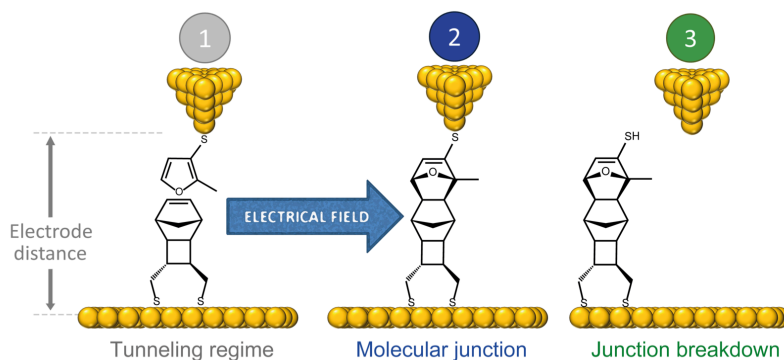


Figure 1. Diels-Alder Reaction in an Electric Field

1. (a) For a review see: S. Shaik, D. Mandal, R. Ramanan, *Nature Chem.* **2016**, 8, 1091-1098; (b) R. Meir, H. Chen, W. Lai and S. Shaik, *ChemPhysChem*, **2010**, 11, 301–310
2. A. C. Aragonès, N. L. Haworth, N. Darwish, S. Ciampi, N. J. Bloomfield, G. G. Wallace, I. Diez-Perez and M. L. Coote, *Nature* **2016** 531, 88-91
3. (a) G. Gryn'ova, D.L. Marshall, S.J. Blanksby and M. L. Coote *Nature Chem.* **2013**, 5, 474-481. (b) G. Gryn'ova and M.L. Coote *J. Am. Chem. Soc.* **2013**, 135, 15392-15403. (c) M. Klinska, L. M. Smith, G. Gryn'ova M. G. Banwell and M. L. Coote, *Chem. Sci.* **2015**, 6, 5623–5627.