
Directionality and the Role of Polarization in Electrostatic Catalysis

*Michelle L. Coote**

Research School of Chemistry, Australian National University, Canberra, AUS

**Michelle.Coote@anu.edu.au*



*Michelle Coote
presenting author*

Abstract

It is well known that the rate of redox reactions can be manipulated by means of an electrical potential gradient. However, as elegantly demonstrated by Shaik and co-workers, external electric fields should be able to catalyse non-redox processes also, by electrostatically stabilizing the dipoles associated with charge-separated valence bond contributors of transition states, and hence enhancing resonance and lowering the barrier [1]. However, since these effects are directional in nature, implementing electrostatic catalysis in practice has been a challenge. Recently we have addressed this problem, and experimentally demonstrated practical electrostatic catalysis using two complementary approaches. First, we have used charged functional groups on the substrate, auxiliary or catalyst to deliver a localized oriented electric field that can be modulated by simple pH changes [2]. Second, with collaborators, we have used various surface chemistry techniques to control the orientation of reagents in an external electric field [3]. Interestingly, our own theoretical studies of some of these systems indicate that, due to polarization, electrostatic effects on reaction barriers and enthalpies actually have a significant non-directional component [4]. This suggests we may one day be able to design reactions where alignment in an electric field is not necessary for catalysis, thus broadening its scope. This presentation will briefly outline our progress toward practical electrostatic catalysis, but with a focus on the role of polarization in determining the strength of these effects.

Reference and notes

- [1] S. Shaik, D. Mandal, R. Ramanan, *Nat. Chem.* 2016, 8, 1091-1098
- [2] G. Gryn'ova, D.L. Marshall, S.J. Blanksby, M.L. Coote, *Nat. Chem.*, 2013, 5, 474-481; M. Klinska, L. M. Smith, G. Gryn'ova, M.G. Banwell, M.L. Coote, *Chem. Sci.*, 2015, 6, 5623-5627; G. Gryn'ova, L.M. Smith, M.L. Coote, *Phys. Chem. Chem. Phys.*, 2017, 19, 22678-22683; H.M. Aitken, M.L. Coote, *Phys. Chem. Chem. Phys.*, 2018, 20, 10671-10676.
- [3] A. Aragones, N. Haworth, N. Darwish, et al., *Nature*, 2016, 531, 88-91; L. Zhang, E. Laborda, N. Darwish, et al. *J. Am. Chem. Soc.*, 2018, 140, 766-774.
- [4] G. Gryn'ova, Coote, *J. Am. Chem. Soc.*, 2013, 135, 15392-15403; & *Aust. J. Chem.*, 2017, 70, 367-372.