

Demonstration of pH-dependent electrostatic catalysis in radical reactions

It is normally assumed that the ability to use electric fields to accelerate chemical reactions is limited to redox processes occurring at electrode surfaces. However, electric fields should theoretically be able to catalyse non-electrochemical reactions by electrostatically stabilising high-energy charge-separated resonance contributors to the reaction's transition state. In practice, the challenge is orienting the field relative to the reaction centre. One solution is to use charged functional groups within the substrate, auxiliary or catalyst whose electric field is relatively localised but can be precisely aligned with respect to the reaction centre. If the charged functional group is an acid/base group, this approach has the added advantage of incorporating a pH switch for the catalytic effects. Researchers from the Australian National University have now provided a proof-of-concept of pH-dependent electrostatic catalysis by demonstrating a pH switch of up to two orders of magnitude on the rate and equilibrium constant for hydrogen atom transfer between a hydroxyl amine bearing a non-conjugated carboxylic acid and a reference profluorescent nitroxide radical (Klinska M., Smith L.M., Gryn'ova G., Banwell M.G., Coote M.L., *Chem. Sci.* 2015, doi: 10.1039/C5SC01307K). Deprotonation of the carboxylic acid stabilises the resulting nitroxide radical anion, favouring the forward reaction. This ability to manipulate nitroxide stability via a simple pH switch opens the way to the possible use of this effect in synthetic and polymerisation processes.

