

Electrostatic Catalysis of Chemical Reactions

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Chemists appreciate that the rate of redox reactions can be manipulated by means of an electrical potential gradient. However, it was only recently that it was shown that an external electric field can also be used to catalyse non-redox reactions, thereby opening up a new dimension to chemical catalysis [1]. So-called electrostatic catalysis arises because most chemical species have some degree of polarity and so can be stabilized by an appropriately aligned electric field; when this occurs to a greater extent in transition states compared with reactants, reactions are catalysed [2]. However, by their nature such effects are highly directional and so implementing them in practical chemical systems is problematic. We have been using a combination of theory and experiment to explore various solutions to this problem. The first is using surface chemistry techniques, in conjunction with the break-junction technique in scanning tunnelling microscopy [1]. This allows us to detect chemical reaction events at the single molecule level, whilst delivering an oriented electrical field-stimulus across the approaching reactants. The second is making use of the electric fields within the double layers of electrochemical cells to manipulate both redox and non-redox unimolecular reactions. Here we find that molecules actually self-align and interact with electrolyte ions to facilitate catalysis [3]. Finally, in an approach that is truly scalable, 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 [4]. 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 latest results will be presented and the prospects for electrostatic catalysis discussed.

References

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