July 16-21, 2017 at UC San Diego, CA, USA

Design of Novel Asymmetric Autocatalytic Systems

R. J. H. Scanes[1] and S. P. Fletcher[1]

[1]Chemical Research Laboratory, Department of Chemistry, University of Oxford, 12 Mansfield Rd, Oxford, OX1 3TA, UK
* stephen.fletcher@chem.ox.ac.uk

Introduction: The origin of chemical asymmetry in life is unknown, with asymmetric autocatalysis a prevalent concept put forward to explain this.[1][2] Despite this asymmetric autocatalytic reactions are rare, the Soai reaction being the only conclusive example, in which the chiral products which increase in enantiopurity over time.[3]

Nonlinear effects in asymmetric catalysis: Here we discuss the design novel asymmetric autocatalytic reactions, based on modes of catalysis distinct from the Soai reaction, which share common principles. Essential to asymmetric autocatalysis is the notion of minor enantiomer inactivation, leading to nonlinear effects. Based on early work by Frank, Blackmond describes how monomeric autocatalysts would not be expected to enantioenrich without some suppression of the catalytic activity of the minor enantiomer.[4][5] In the case of Soai's system nonlinear effects arise from catalytically active dimers and higher aggregates.[6]

It is generally acknowledged there is little direct prebiotic relevance to the Soai reaction, due to the highly specific conditions required. In contrast, organocatalysis, in which organic small molecules aid the production of others, often shows relatively low air and water sensitivity, important considerations in prebiotic chemistry and many asymmetric transformations are known.[7][8] Although many systems displaying nonlinear effects have been found, the interactions causing these effects are often poorly understood and examples in the field of organocatalysis are rare.[9] Here we discuss investigation into nonlinear effects in known organocatalytic reactions. The results of this will inform the design of potential autocatalytic systems.

[1] Feringa BL and van Delden RA (1999) *Angewandte Chemie International Edition* 38:3418–3438. [2] Blackmond DG (2010) *Cold Spring Harbor Perspectives in Biology* 2:a002147. [3] Soai K et al. (1997) *Nature* 378:767–768. [4] Frank FC (1953) *Biochimica et Biophysica Acta* 11:459–463. [5] Blackmond DG (2004) *Proceedings of the National Academy of Sciences of the United States of America* 101;5732–5736. [6] T. Gehring et al. (2010) *Chirality* 22:E173–E182. [7] Sigman MS, Vachal P and Jacobsen EN (2000) *Angewandte Chemie International Edition* 39:1279–81. [8] Okino T, Haoshi Y and Takemoto Y (2003) *Journal of the American Chemical Society* 125:12672–12673. [9] Noble-Terán ME et al. (2016) *ChemCatChem*, 8:1836–1845.