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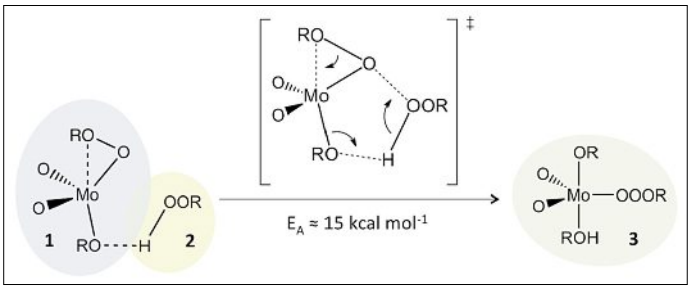
Swiss Science Concentrates

A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

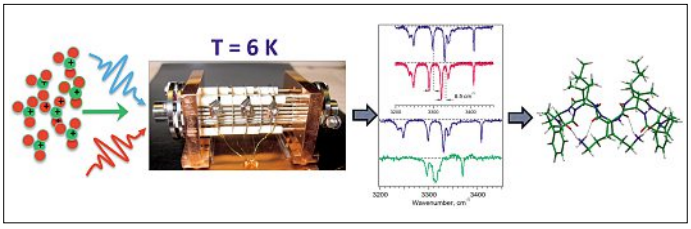
Catalytic Epoxidations with Peroxides: Molybdenum Trioxide Species as the Origin of Allylic Byproducts

U. Neuenschwander, E. Meier, and I. Hermans*, *Chem. Eur. J.* **2012**, *18*, 6776.
ETH Zürich
Catalytic epoxidations provide versatile building blocks for the synthesis of value-added products. The authors investigated the Mo^{VI}-catalyzed olefin epoxidation using alkyl hydroperoxides. The molybdenum(IV)peroxide (**1**) is the key intermediate, generated by reaction of Mo^{VI} with the peroxide. In addition to the desired Chong-Sharpless epoxidation mechanism, a competing reaction of **1** with additional peroxide (**2**), yielding molybdenum(VI)trioxide (**3**) is described. This trioxide readily decomposes to radicals under the reaction conditions, reducing the epoxide selectivity. The reaction pathways were characterized using DFT calculations, providing kinetic parameters that are in good agreement with the experimental observations.



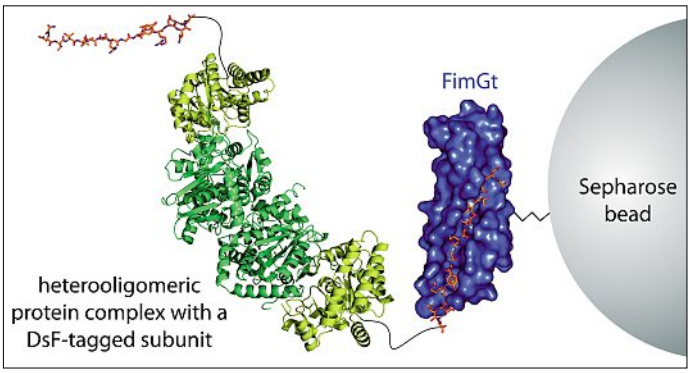
Interplay of Intra- and Intermolecular H-Bonding in a Progressively Solvated Macrocyclic Peptide

N. S. Nagornova, T. R. Rizzo, and O. V. Boyarkin*, *Science* **2012**, *336*, 320.
EPF Lausanne
Hydrogen bonds are critical to the structure and functionality of biomolecules. Scrutinizing the delicate balance between inter- and intramolecular H-bonds is challenging because of their inherent transient- and inhomogeneous character. To address this, Boyarkin and coworkers report on a detailed IR-UV study of a cold macrocyclic decapeptide, antibiotic gramicidin S. Upon titration with water molecules (1 to 50), they were able to resolve by spectroscopy the subtle structural changes associated with bound water molecules. With this technique they scrutinized the most stable water binding sites and the nature of H-bonding network that grows as the number of water molecules are introduced.



The Most Stable Protein-Ligand Complex: Applications for One-Step Affinity Purification and Identification of Protein Assemblies

C. Giese, F. Zosel, C. Puorger, and R. Glockshuber, *Angew. Chem. Int. Ed.* **2012**, *51*, 4474.
ETH Zürich
Protein over-expression and purification is one of the most important workhorses in molecular biology. Several affinity chromatography methods (*e.g.* cmyc, FLAG and His_6 tags) are used routinely to purify recombinant proteins. For low abundance proteins, affinity chromatography is often problematic however. Glockshuber and co-workers report on an affinity purification system based on adhesive type 1 pili from *E. coli*, a rigid, filamentous, supramolecular protein complex. The noncovalent interaction between the truncated pilus subunit FimGt and a peptide corresponding to the 15 N-terminal amino acids of the neighboring subunit FimF (DsF) displays the lowest dissociation constant of a protein-ligand complex reported so far with a $K_D = 1.5 \cdot 10^{-20}$ M. FimGt covalently attached to Sepharose can thus be used to specifically immobilize recombinant proteins bearing a DsF-tag. Subsequent cleavage of the DsF-tag allows for the single step purification of proteins and protein complexes directly from cell extracts with excellent purity and recovery rates. Thus, the FimGt/DsF system is a promising generic tool for multiple applications in biotechnology such as the identification of the components of heterooligomeric protein complexes in pull-down assays or the permanent and functional immobilization of DsF-tagged targets on a FimGt-covered support.



Prepared by Nico Bruns, Adnan Ganic, Valentin Köhler, Fabien Monnard, Mark Ringenberg and Thomas R. Ward
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