



Swiss Science Concentrates

A CHIMIA Column

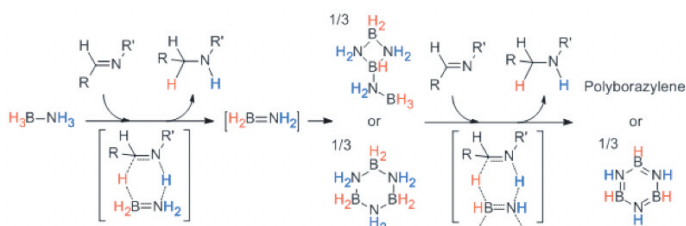
Short Abstracts of Interesting Recent Publications of Swiss Origin

Transfer Hydrogenation of Imines with Ammonia-Borane: A Concerted Double-Hydrogenation-Transfer Reaction

X. Yang, L. Zhao, T. Fox, Z.-X. Wang, and H. Berke, *Angew. Chem. Int. Ed.* **2010**, *49*, 2058

University of Zurich and Graduate University of Chinese Academy of Sciences

Ammonia-borane ($\text{H}_3\text{N}-\text{BH}_3$) is considered a feasible material for chemical hydrogen storage due to its potentially very high storage capacity (19.6 weight% H). Herein, this reagent was used for metal-free direct transfer hydrogenations of various imines which proceeded under mild conditions. The results of deuterium labeling studies, primary deuterium kinetic isotope effects, Hammett correlations and DFT calculations were all supportive of a concerted double-hydrogen-transfer mechanism.

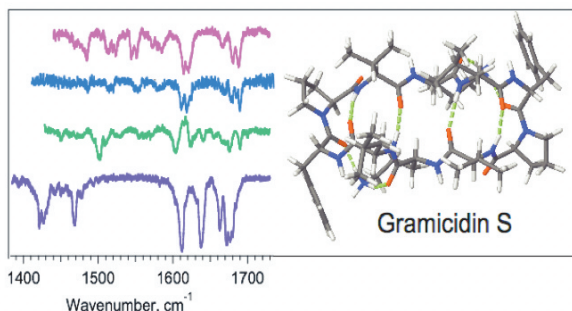


Highly Resolved Spectra of Gas-Phase Gramicidin S: A Benchmark for Peptide Structure Calculations

N. S. Nagornova, T. R. Rizzo, and O. V. Boyarkin*, *J. Am. Chem. Soc.* **2010**, *132*, 4040

EPFL

The authors report vibrationally resolved UV spectrum of doubly protonated gramicidin S (GS) in the gas phase and, subsequently, a highly resolved, conformer-specific IR spectrum in the $6 \mu\text{m}$ fingerprint region, using a cold ion trap in combination with table-top lasers. The study has revealed at least three conformational states of GS populated under our experimental conditions, with the major one showing evidence of a symmetric (C_2) structure similar to that in the condensed phase. The derived qualitative constraints, along with the measured vibrational frequencies, serve as a benchmark for computations of peptide structure.

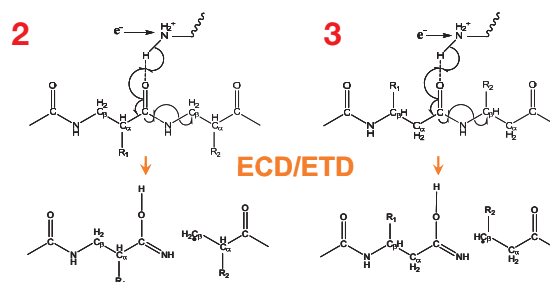


Radical Stability Directs Electron Capture and Transfer Dissociation of β -Amino Acids in Peptides

H. B. Hamidane, A. Vorobyev, M. Larregola, A. Lukaszuk, D. Tourwé, S. Lavielle, P. Karoyan, and Y. O. Tsybin, *Chem. Eur. J.* **2010**, *16*, 4612

EPFL, Université Pierre et Marie Curie and Vrije Universiteit Brussel

This paper describes the characteristics of the radical-ion-driven dissociation of β^2 - and β^3 -amino acids incorporated into α -peptides at a single or multiple positions, as probed by electron-capture and electron-transfer dissociation (ECD/ETD) tandem mass spectrometry (see Fig.). The radical stability of amino acid side chains dominates the nearby peptide backbone bond rupture of β -amino acids in ECD/ETD to a substantially larger extent than it does with α -amino acids.



An Atomistic Picture of the Regeneration Process in Dye Sensitized Solar Cells

F. Schiffmann, J. VandeVondele*, J. Hutter, A. Urakawa, R. Wirz, and A. Baiker, *PNAS*, **2010**, *107*, 4830

University of Zurich and ETH Zurich

In this article, the authors have identified a highly efficient mechanism for the regeneration of *cis*-bis(isothiocyanato)bis(2,2-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) sensitizing dye by I^- using molecular dynamics simulations based on density functional theory. Among the different results, they found that barrier-free complex formation of the oxidized dye with both I^- and I_2^- , and facile dissociation of I_2^- and I_3^- from the reduced dye are key steps in this process. Also, *in situ* vibrational spectroscopy confirms the reversible binding of I_2 to the thiocyanate group of the reduced dye.

