In metal-free enzymes, catalysis can be effected by the formation of covalent intermediates (such as enamines in class I aldolases), and by hydrogen bonding networks. In the latter case, the lowering of activation barriers results (inter alia) from the stabilization of developing charges (e.g. by the “oxy anion hole” in serine hydrolases), the facilitation of proton translocations, or the polarization of nucleophilic/electrophilic reaction partners.

Numerous examples exist how enzymatic “covalent organocatalysis”\(^{1a}\) can be mimicked by low-molecular weight organocatalysts. Prominent examples are proline-catalyzed aldol and Michael-reactions (via enamines), iminium ion catalysis in cycloadditions, acylpyridinium ions in acyl transfer reactions etc.. On the other hand, the design of “non-covalent” organocatalysts, acting solely by hydrogen bonding, is a new and emerging branch of (biomimetic) organocatalysis.\(^{1b, c}\)

The lecture will present four examples of non-enzymatic (but in some cases enzyme-like!) catalysis effected by hydrogen bonding networks: (i) epoxidation of olefins and Baeyer-Villiger oxidation of ketones with \(\text{H}_2\text{O}_2\) in fluorinated alcohol solvents;\(^2\) (ii) peptide-catalyzed asymmetric epoxidation of enones by \(\text{H}_2\text{O}_2;\(^3\) (iii) dynamic kinetic resolution of azlactones, affording enantiomerically pure \(\Lambda\)-amino acids;\(^4\) (iv) kinetic resolution of oxazinones, affording enantiomerically pure \(\Delta\)-amino acids.\(^5\) All four types of transformations are of preparative value, and their scope and mechanisms are discussed.
References:


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gez. Prof. Dr. Thomas Koop, Prof. Dr. Jochen Mattay, Prof. Norbert Sewald