HR-MAS NMR in Organocatalysis: *In situ* Observation of the Juliá-Colonna Epoxidation Catalyzed by Oligopeptide Gels

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For the enantioselective epoxidation of electron-deficient alkenes, the three phase system developed by Juliá and Colonna for chalcon-type olefines, utilizing homo-oligopeptides in the presence of base and hydrogen peroxide as catalysts, has proven to be the most powerful method.[1] The long-standing debate of the mechanism of this reaction[2] has been complicated by the properties of the reaction mixture, a solid-aqueous-organic slurry, which so far excluded the use of high resolution liquids NMR for studies.

In our study, we employed HR-MAS techniques for the *in situ* NMR monitoring of the reaction. The highly resolved spectra yielded by this approach allowed us to apply a range of standard NMR techniques (COSY, NOESY, relaxation measurements) for the observation of the progress and possible intermediates of the reaction. Also, the successful implementation of saturation transfer difference spectroscopy (STD) to this system is reported.

One of the most challenging tasks for the mechanistic investigation of the Juliá-Colonna epoxidation by NMR could be solved by elaborating a protocol for the performance of the reaction in a solid state rotor. For the first time HR-MAS NMR studies of the catalytically active species present in the Juliá-Colonna reaction were accomplished. Our studies of poly-*L*-leucine gels not only allowed the *in situ* observation of the reaction, but also the study of chalcon poly-*L*-leucine interactions. From the combination of NOE, relaxation and STD experiments, the mode of action of base, hydrogen peroxide and phase transfer catalyst could be highlighted.

[1] Juliá, S.; Masana, J.; Vega, J.C., *Angew. Chem. Int. Ed.*, **1980**, *19*, 929-931.
[2] Berkessel, A.; Gasch, N.; Glaubitz, K.; Koch, C., *Org. Lett.*, **2001**, *3*, 3839-3842.; Kelly, D. R.; Roberts, S. M., *Chem. Commun.,* **2004**, 2018-2020.; Mathew, S. P.; Gunathilagan, S.; Roberts, S. M.; Blackmond, D. G., *Org. Lett*,. **2005**, *7*, 4847-4850.