

P1.5 Coupled operando NMR and UV-vis spectroscopy of CO₂ activation reactions

Topic and overall goal. The study of reaction mechanism strongly relies on the acquisition of meaningful experimental data that mirror the processes occurring at the molecular level, i.e., the elementary steps of a catalytic cycle. Although this is difficult to realise due to the short-lived nature of intermediates, the typically low catalyst concentrations, or the technical limitations of certain spectroscopies, several approaches were described in the past that allow for the real-time monitoring of catalytic reactions using well-established spectroscopic techniques such as NMR, UV-Vis, EPR, or vibrational spectroscopy. The implementation of low-cost, compact instruments would be of particular interest to allow non-expert users to monitor reactions in the environment of a standard preparative laboratory. The changes of spectra with time and concentration of compounds call for chemometric analysis which can extract and assign spectral signatures to specific species and to determine the concentrations of these species in dependence of the considered parameters.¹ In the past this has been demonstrated by the Neymeyr group for simple organic transformations.² A setup for low-field benchtop ¹H and ³¹P NMR spectroscopy in flow mode that can be used for non-invasive monitoring of stoichiometric and catalytic transformations involving highly sensitive transition metal complexes is available in the Beweries group.³ Furthermore, the use of UV-Vis spectroscopic data to determine catalytic rates and stability constants is a well-established approach that was successfully used at LIKAT in the past.⁴

Specific aims and work plan. In this project we aim to apply the established benchtop low-field NMR setup to monitor stoichiometric and catalytic organometallic transformations involving CO₂ in flow mode. Addition of CO₂ can be realised at pressures of up to 4 bar using the flow NMR setup, consisting of a customised reaction vessel, the NMR device, and a flow system (including a flow cell, filters, and a microgear pump). Alternatively, reactions at ambient pressure can be monitored using a well-established fully automatic gas buret that was designed and applied for monitoring hydrogen uptake and evolution.⁵ Implementation of this setup into the NMR flow scheme will be part of the PhD project. Combination of standard and stopped-flow UV-Vis and volumetric analysis was done in the group in the past. This approach will be used for kinetic and mechanistic analysis of reductive CO₂ coupling as well. Ultimately, we plan to design and apply a setup that combines low-field flow NMR and UV-Vis spectroscopy, as well as volumetric analysis of CO₂ uptake. Coupling of insensitive low-field NMR spectroscopy and highly sensitive UV-Vis spectroscopy can be achieved by bypassing reaction solutions from the flow system or by using suitable optrodes immersed into a customised reaction vessel. Spectroscopic data generated in this project are to be analysed by the Neymeyr group using suitable chemometric tools to obtain information on the presence of individual components involved and derive kinetic data.

Within this project the PhD student will receive training in the fundamentals of NMR and UV-Vis spectroscopy, will gain knowledge in the design of suitable setups for spectroscopic reaction monitoring and will perform kinetic studies that are required for mechanistic analysis of small molecule activation reactions.

Connection within the RTG. This PhD project will be jointly supervised by Torsten Beweries and Klaus Neymeyr. Within the RTG there will be a close collaboration with the Beller (homogeneous catalysis, CO₂ chemistry), Brückner, and Ludwig group (general aspects of operando spectroscopy).

- 1 M. Sawall, H. Schröder, D. Meinhardt, K. Neymeyr, In *Comprehensive Chemometrics: Chemical and Biochemical Data Analysis*; Brown, S., Tauler, R., Walczak, B., Eds., Elsevier, **2020**; 199-231.
- 2 D. Meinhardt, H. Schröder, J. Hellwig, E. Steimers, A. Friebel, T. Beweries, M. Sawall, E. von Harbou, K. Neymeyr, *J. Magn. Res.* **2022**, 339, 107212.
- 3 a) L. Tadiello, H.-J. Drexler, T. Beweries, *Organometallics* **2022**, 41, 2833-2843; b) N. Jannsen, C. Fischer, C. Selle, C. Pribbenow, H.-J. Drexler, F. Reiß, T. Beweries, D. Heller, *Dalton Trans.* **2022**, 51, 18068-18076.
- 4 H.-J. Drexler, A. Preetz, T. Schmidt, D. Heller, *Kinetics of Homogeneous Hydrogenations: Measurement and Interpretation. In Handbook of Homogeneous Hydrogenation*, ed. J. G. de Vries, C. J. Elsevier, Wiley-VCH, Germany, 2007, ch. 10, vol. 1, pp. 257-293
- 5 T. Beweries, J. Thomas, M. Klahn, A. Schulz, D. Heller, U. Rosenthal, *ChemCatChem* **2011**, 3, 1865-1868.