

P1.6 Mechanistic operando IR studies of oxalate formation with transition metal complexes

Topic and overall goal. The aim of this PhD project is the elucidation of mechanistic and kinetic aspects of the formation of oxalate via CO₂ coupling with transition metal complexes by in-situ/operando infrared spectroscopy under ambient and high-pressure. The combination of spectroscopic experiments and chemometrics will be used to identify and quantify relevant organometallic species. Extensive characterizations of complexes by multiple spectroscopic methods and kinetic investigations will provide in-depth structure-reactivity relationships.

Specific aims and work plan. The formation of oxalate complexes from the reductive coupling of CO₂ with early and late transition metal complexes in the presence of a reductant will be studied in a time-resolved manner (time intervals in the msec – min range) by in-situ/operando FTIR spectroscopy.^{1,2,3,4} With the help of advanced numeric tools for chemometric data analysis, developed by the Neymeyr group, pure component spectra of involved species and concentration profiles will be extracted from the spectral-time series. The interpretation of experimental spectra for resting states as well as intermediates and assignment to molecular structures will be supported by vibrational analyses via DFT-methods and isotopic labelling using ¹³CO₂.^{5,6} Complementary methods such as NMR, UV-vis and Raman spectroscopy will be used for a comprehensive structural characterization. Model compounds prepared from transition metal halides with respective oxalate salts will be used as reference materials. Within extended kinetic studies the influence of crucial parameters (temperature, pressure, concentrations) on the reaction rate will be explored in detail with respect to the conformation of a mechanistic hypothesis. Kinetic modelling to derive rate and equilibrium constants will be conducted, supported by model simulations. This approach will be applied to study the coordination mode of CO₂ at the metal centre, the reductive coupling to oxalate as well as its removal in the presence of reduction equivalents and electrophiles for a selected variety of early transition metal complexes (e.g., Ti, Zr, V) developed by the Bawerles group in P1.3.⁷ The effect of different reductants, additives and solvents will be explored. Reductive coupling towards oxalate will be monitored using model methoxycarbonyl and hydroxycarbonyl complexes of late transition metals (e.g., Mn, Fe, Ru, Pd, Pt) provided by the Beller group in P1.1 and P1.2. Operando IR will be used to monitor molecular structure and reactivity within individual steps of insertion and oxidative addition followed by reductive coupling.

The PhD student will be trained handling of sensitive organometallic compounds during spectroscopic investigations and time-resolved reaction monitoring using mainly operando FTIR, supported in selected cases also by Raman, NMR and UV-Vis spectroscopy, chemometric data analysis, kinetic modelling and DFT calculations.

Connection within the RTG. The PhD student will be jointly supervised by Prof. Angelika Brückner and Prof. Ralf Ludwig. Strong collaborations will take place within the RTG between the groups of Prof. Beller (late transition metals complexes), Prof. Bawerles (early transition metal complexes) and Prof. Neymeyr (chemometrics, MCR methods).

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- 1 H.-Q. Liang, T. Bawerles, R. Francke, M. Beller, *Angew. Chem. Int. Ed.* **2022**, 61, e202200723.
 - 2 M. Marx, H. Frauendorf, A. Spannenberg, H. Neumann, M. Beller, *JACS Au* **2022**, 2, 731-744.
 - 3 B. J. Cook, G. N. Di Francesco, K. A. Abboud, L. J. Murray, *J. Am. Chem. Soc.* **2018**, 140, 5696-5700.
 - 4 T. T. Adamson, S. P. Kelley, W. H. Bernskoetter, *Organometallics* **2020**, 39, 3562-3571.
 - 5 Y. Yang, Y. Zhou, X. Jin, G. Wang, M. Zhou, *Phys. Chem. Chem. Phys.* **2022**, 24, 13149-13155.
 - 6 J. Mascetti, F. Galan, I. Pápai, *Coord. Chem. Rev.* **1999**, 190-192, 557-576.
 - 7 N. Hazari, J. Heimann, in *Comprehensive Coordination Chemistry III* (Eds.: E. C. Constable, G. Parkin, L. Que Jr), Elsevier, Oxford, **2021**, pp. 959-975.