

3.3 Mass Spectrometry (W. Schrader)

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During the last three years the MS group had to integrate four new technicians who replaced four retired co-workers with – combined – more than 130 years of experience. Fortunately, the positions could be filled in advance which allowed for some overlap. The training of the new members in all aspects of mass spectrometry therefore was and will be a major part of the internal work.

Additionally, older instruments such as two 30 years old sector field mass spectrometers were replaced by more powerful new instrumentation. These old machines had been used for standard measurements using Electron Ionization (EI) on thermally stable compounds. We now use another sector field instrument for this task while a new high resolution Orbitrap Mass Spectrometer coupled to a gas chromatograph was purchased for high resolution and high accuracy EI measurements.

Likewise, an older FT-ICR MS was decommissioned after the vendor took it out of support (with expensive repairs necessary to keep it running after the magnet had quenched). A new Q-Exactive Orbitrap was purchased in 2014 with an Electrospray Ionization (ESI) source as replacement.

Modern analytical methodologies need to be available in order to solve the analytical problems of the synthetic laboratories. The group is offering full support for all groups at both institutes on campus concerning the identification of unknown and new components using all available ionization methods. Rapid turn-over is a strong priority that allows the synthetic chemists to obtain the results as soon as possible. The institute's own database and software package (MassLib) is constantly modernized to meet new requirements, and the different new atmospheric pressure ionization and high resolution methods have found a greater emphasis.

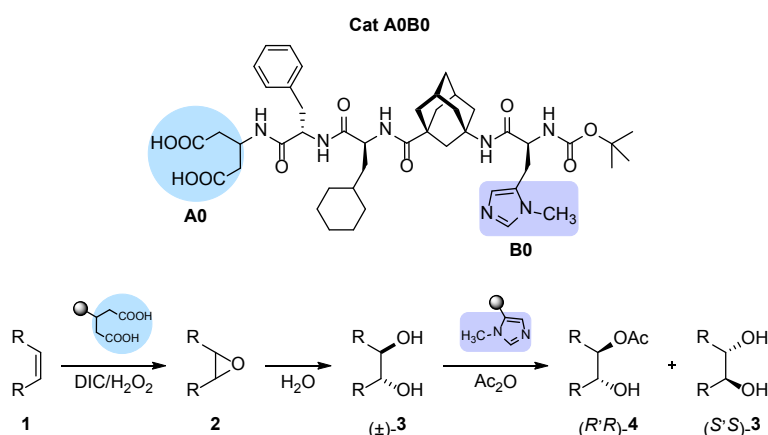


Fig. 1. Reaction sequence using a multicatalyst.^[8]

their mechanisms. One example is a cooperation with the group of Peter Schreiner at the University Giessen. The group has developed a new approach to cascade reactions in organocatalysis, where the different catalytic moieties are attached to a spacer molecule. Each moiety needs activation prior to its reaction in the sequence. We studied the mechanism of one of those reaction sequences, involving a multi-catalyst with a chiral peptide backbone and an adamantane spacer separating two catalytically active centers. One catalytic moiety, a dicarboxylic acid is responsible for the first reaction step, an epoxidation, while an *N*-methyl imidazole moiety catalyzes the terminal acylation step (see Figure 1).^[8]

This triple cascade sequence constituted of an epoxidation, an epoxide opening, and an enantioselective acylation reaction catalyzed by an oligopeptide multicatalyst was studied in detail using electrospray ionization mass spectrometry. The key reaction intermediates were successfully characterized. Additional side reactions were discovered that were not known before. During the activation of the first catalytic moiety by DIC (*diisopropylcarbodiimid*) and H₂O₂ a side reaction takes place on the catalytic moiety for the second reaction step to form a partially oxidized methyl imidazole moiety, which reduces the activity of the second catalytic moiety. These results allow for an optimized reaction planning.

Another project deals with the investigation and characterization of complex crude oil mixtures. Despite the continuous development of renewable energy sources, energy supplies will be dependent upon the availability of fossil materials for at least the next 2-3 decades.

The **research interests** are ranging from the development of analytical techniques to studying complex chemical reactions, often in energy-related materials such as biofuels or fossil fuels. Additional studies focus on the investigation of unusual reactions to gain information about

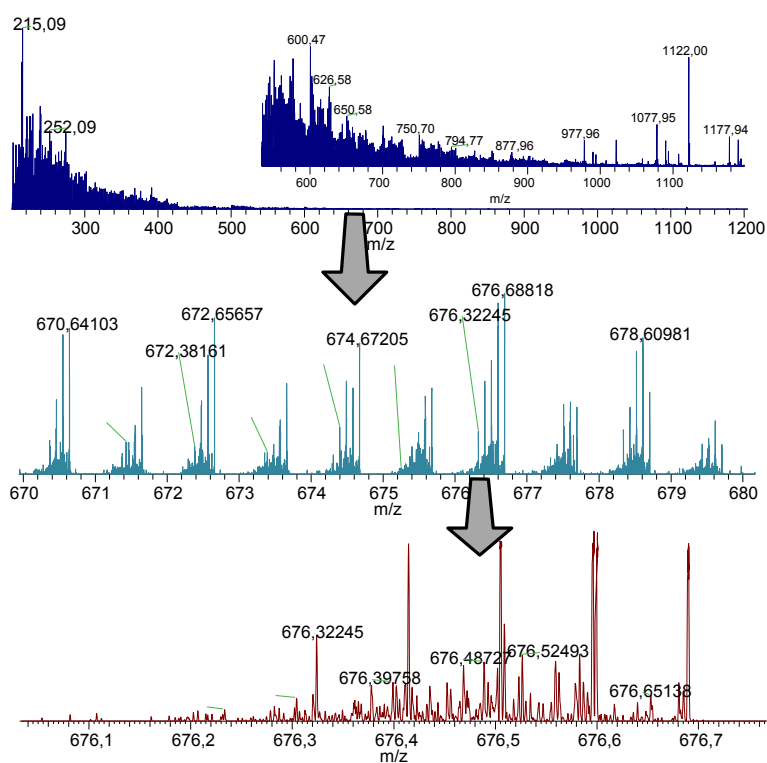


Fig. 2. Mass spectrum with different zoom factors showing the complexity of a crude oil sample.

Even now, as more sustainable resources are mixed with fossil oils, the chemistry in such mixtures still remains a big mystery. One of the reasons is that chemical changes within a mixture of more than one million distinct chemical compounds are almost impossible to follow. Here, ultrahigh resolution mass spectrometry is the only method that allows different components to be distinguished. An example is shown in Figure 2, where a mass spectrum with different zoom factors is shown. It can be seen that up to 200 different signals can be detected and assigned with an elemental composition within one nominal mass unit, describing the complexity of such materials. Since mass spectrometry only gives detailed data of the elemental composition of each signal, chemical diversity such as structural differences of the same elemental formula are not detected. To be able to do this, different hyphenated methods have been developed during the reporting period. These include the online-coupling of ligand exchange chromatography (LEC), size exclusion chromatography (SEC) and ion mobility spectrometry (IMS) to mass spectrometry.

The LEC columns are synthesized and packed in our lab and allow running different separation applications from heavy asphaltenes to full crude oils. Ion mobility spectrometry is a method that separates ionized compounds according to their collisional cross section in an electric field and therefore enables isomeric compounds to be distinguished. Different ion sources for atmospheric pressure photo and laser ionization (APPI and APLI) have been constructed for ionization with an IMS unit coupled to a mass spectrometer. These methods allow isomers within the distinct elemental compositions to be distinguished.

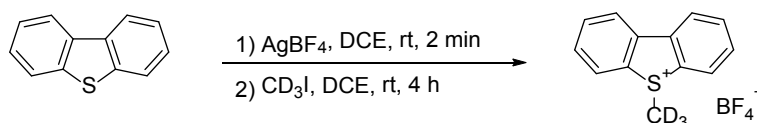


Fig. 3. Alkylation of sulfur heterocycles.

In addition to the development of analytical methods for the analysis of complex mixtures, the chemical reactivity of individual compounds within such complex mixtures has been studied. Estimates show that crude oil contains more than one million chemical compounds which often have some type of aromatic core with a number of different, mostly aliphatic side chains. We have studied the reactivity of the different aromatic cores, specializing on polyaromatic heterocycles and their reactivity towards alkylation. The use of a deuterated alkylating agent allows differentiation of alkylated and non-alkylated compounds on the molecular level using mass spectrometry.^[9]

Publications resulting from this research area:

- (1) Schrader, W. *Eur. J. Mass Spectrom.* **2014**, *20*, 0-0.
- (2) Schrader, W.; Xuan, Y.; Gaspar, A. *Eur. J. Mass Spectrom.* **2014**, *20*, 43-49.
- (3) Lababidi, S.; Schrader, W. *Rapid Commun. Mass Spectrom.* **2014**, *28*, 1345-1352.
- (4) Molnárné Guricza, L.; Schrader, W. *J. Mass Spectrom.* **2015**, *50*, 549-557.
- (5) Lim, I.; Schrader, W.; Schüth, F. *Chem. Mater.* **2015**, *27*, 3088-3095.
- (6) Vetere, A.; Schrader, W. *Anal. Chem.* **2015**, *87*, 8874-8879.
- (7) Molnárné Guricza, L.; Schrader, W. *Energy Fuels* **2015**, *29*, 6224-6230.
- (8) Alachraf, M. W.; Wende, R. C.; Schuler, S. M. M.; Schreiner, P. R.; Schrader, W. *Chem.-Eur. J.* **2015**, *21*, 16203-16208.
- (9) Wang, X.; Schrader, W. *Int. J. Mol. Sci.* **2015**, *16*, 30133-30143.

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