3.3 Mass Spectrometry (W. Schrader)

In the last three years the focus of the MS group has changed only slightly. The major task is still the service work for the groups of both Max Planck Institutes (Kohlenforschung and Bioanorganische Chemie/Chemical Energy Conversion) on the campus. While the number of samples measured for the BAC/CEC decreased in the last years this has been compensated by a much higher sample emergence from the Kohlenforschung.

Modern analytical methodologies are needed to solve the problems in the synthetic laboratories. This is achieved by providing full support in identifying unknown and new components using all ionization methods available and interpreting the obtained data. Rapid completion is a strong priority that allows the synthetic chemists to obtain the results and implement them into their work. The Institute's own data base and software package (MassLib) is constantly modernized, and different new atmospheric pressure ionization and high resolution methods have found a greater emphasis.

Standard MS: The standard program includes direct evaporation of new volatile and solid synthetic compounds. Pure liquid and volatile compounds are analyzed by direct injection and GC/MS. For polar components electrospray (ESI) MS is the method of choice for many problems.
Special measurements: High resolution mass spectrometry has become an important tool for characterization of newly synthesized compounds. FT-ICR MS is a very accurate and high resolving MS technique that allows for the investigation of a much broader spectrum of samples. The method is especially useful for the investigation of reaction mechanisms, where small intermediates are being observed in order to study how chemical reactions proceed. High-resolution MS/MS data can provide accurate structural information about unknown compounds due to fragmentation and is developing into an important tool for the investigation of chemical reactions.

The **research interests** are focusing on the investigation of complex and unusual reactions to gain information about mechanisms or formation pathways. Very often such reactions cannot be observed because potential intermediates are low in intensity or are available only for a short life-time and here mass spectrometry can play a vital role in characterizing mechanisms. One example is from a project dealing with complex organocatalytic reactions. In this project a complex organocatalytic triple cascade reaction for the stereoselective synthesis of *tetra*-substituted cyclohexene carbaldehydes

(cooperation with D. Enders within the DFG Priority Program *Organocatalysis*) was investigated (see Figure 1). The cascade starts with the activation of an aldehyde **1** by enamine formation thus allowing its addition to a nitroalkene **2** via a Michael reaction. The liberated catalyst from the hydrolysis process forms an iminium ion of an α,β-unsaturated aldehyde **3** to accomplish the conjugate Michael addition with the nitroalkane **7**. In subsequent steps, the enamine **9** leads to an intramolecular aldol condensation via **10**. The final product tetra-substituted cyclohexene carbaldehyde **11** is obtained after hydrolysis. [10]

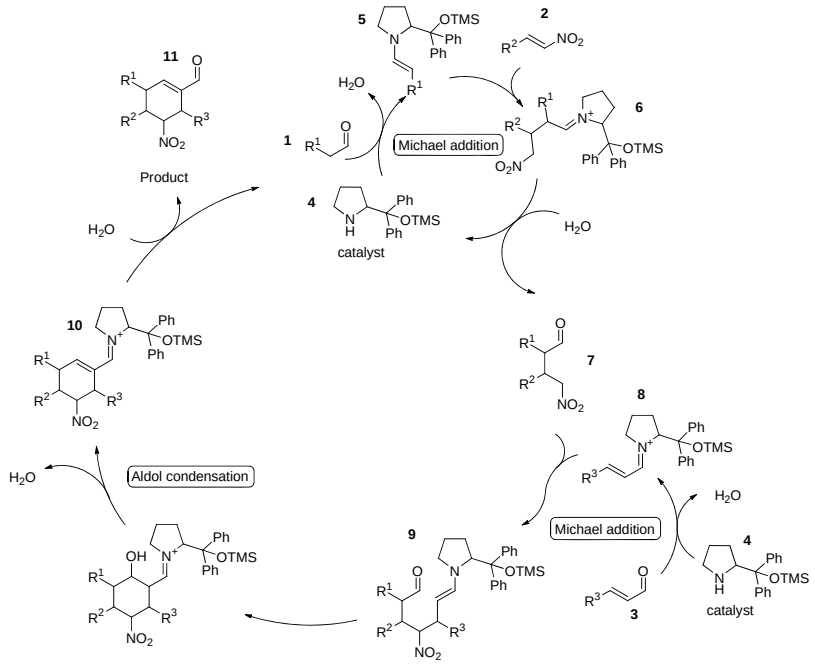

Figure 1: The proposed catalytic cycle for the complex organocatalyzed triple cascade reaction.

The intermediates of the triple cascade reaction have been intercepted through ESI-MS monitoring and structural assignments were aided by using the accurate mass data from FT-ICR MS. For each intermediate structural information was obtained from MS/MS measurements from intercepted components allowing a thorough characterization of the complex reaction. Other cooperations on organocatalytic reactions with B. List and P. Schreiner are not yet finalized.

Another project deals with the investigation, behavior and characterization of complex crude oil mixtures. Despite the continual development of renewable energy sources, energy supplies will be dependent upon the availability of crude oil for at least the next

two decades. As the remaining light crude oils diminish, previously unconventional resources will need to be upgraded into petroleum. Many of the problems associated with recovery, separation or processing of crude oils are related to the presence of high concentrations of heavy components in the crude, like asphaltenes. It was possible to study asphaltenes with a broad set of different ionization methods combined with ultrahigh resolution mass spectrometry (FT-ICR MS).

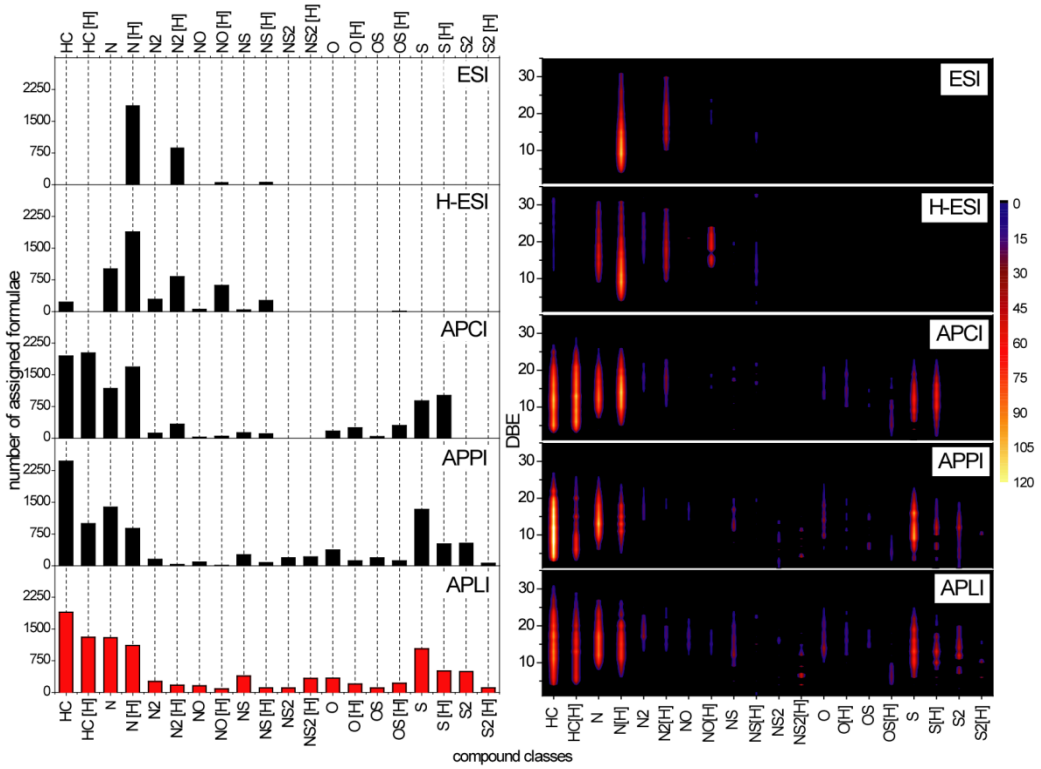

Figure 2: Population based compound classes within the assigned formulae (left) and the DBE distribution of the individual compound classes (right) using ESI (top), H-ESI, APCI, APPI and APLI (bottom) modes, according to the number of assigned molecules.

A mild, REMPI based laser ionization method was compared to electrospray-, chemical- and photo-ionization methods. The populations of the assigned molecules were found to differ substantially for each ionization method, especially in the heteroatomic and in non-heteroatomic content and in aromaticity. In maximum, more than 10,000 different components were detected and assigned for three of the five ionization methods for this asphaltene fraction, thus indicating the real complexity of the whole crude oil. An overview of the different compound classes can be obtained from Figure 2 where different classes and their respective DBE values (the number of double bonds and ring closing bonds within a molecule) are shown. [7]

Another approach of simplifying crude oil measurements was the first reported direct coupling of a normal phase liquid chromatographic separation of crude oil to an ultrahigh resolution MS. The difficulty here is that the concentration used for direct infusion experiments ranges between 100 and 500 ppm of sample. This means that each individual component is available only in minute amounts during the analysis. The mass spectrometric detection is usually carried out by adding between 100 and 500 transients to gain statistical depth. But when using LC/MS the time required to co-add a large number of transients is not available because of the associated loss of chromatographic resolution. On the other hand, when recording the spectra from an LC/MS experiment the sensitivity needs to be high enough that all the components can be detected in each individual scan and the concentration of the sample has to be at an optimum level in order to avoid overloading effects when standard chromatographic columns are used. This is one probable reason why online coupling of LC/MS for crude oil analysis is so difficult and until now all work on separation of crude oil has been done offline by collection of individual fractions. The online coupling was realized here for the group separation of nitrogen containing species using atmospheric pressure laser ionization. [1]

Additionally, the project with the Schüth group on the nucleation behavior of silicates in solution continued (for details see Chapter 2.3.2).

Publications resulting from this research area:

(1) Lababidi, S.; Panda, S.K.; Andersson, J.T.; Schrader, W. *Anal. Chem.* **2013,** 85, 9478−9485.
(2) Lababidi, S.; Panda, S.K.; Andersson, J.T.; Schrader, W. *Energy Fuels* **2013**, 27, 1236−1245.
(3) Lim, I.H.; Schrader, W.; Schüth, F. *Microporous Mesoporous Mater.* **2013**, 16620–36.
(4) Hegazi, A.H.; Fathalla, E.M.; Panda, S.K.; Schrader, W.; J.T. Andersson, *Chemosphere* **2012**, 89, 205–212.
(5) Gaspar, A.; Zellermann, E.; Lababidi, S.; Reece, J.; Schrader, W. *Energy Fuels* **2012**, 26, 3481−3487.
(6) Hagmeyer, D.; Ruesing, J.; Fenske, T.; Klein, H.-W.; Schmuck, C.; Schrader, W.; Minas da Piedaded, M.E.; Epple, M. *RSC Adv.* **2012**, 2, 4690–4696.
(7) Gaspar, A.; Zellermann, E.; Lababidi, S.; Reece, J.; Schrader, W. *Anal. Chem.* **2012**, 84, 5257−5267.
(8) Gaspar, A.; Schrader, W. *Rapid Commun. Mass Spectrom.* **2012**, 26, 1047–1052.
(9) Panda, S.K.; Brockmann, K-J.; Benter, T.; Schrader, W. *Rapid Commun. Mass Spectrom.* **2011**, 25, 2317–2326.

(10) Alachraf, M.W.; Handayani, P.P.; Hüttl, M.R.M.; Grondal, C.; Ender, D.; Schrader, W. *Org. Biomol. Chem.* **2011**, 9, 1047–1053.