

**TITLE**

**“Mechanistic Implications from Reaction Monitoring and Nanomolar Detection”**

**ABSTRACT**

Reaction monitoring using TLC/HPLC/UPLC/LCMS is a routine practice in organic chemistry to determine the reaction progress and kinetics. While off-line monitoring with manual sampling limits the number of data points in the reaction profile, hence the accuracy of kinetic interpretation, on-line/*in-situ* reaction monitoring produces a more complete and real-time picture under actual process conditions. On-line reaction monitoring using NMR spectroscopy represents an invaluable process analytical technique, providing structural information which facilitates both qualitative and quantitative analysis.

Nevertheless, NMR is notoriously known as an insensitive method. It is often a considerable challenge to capture sparse reaction intermediates, let alone transient species. Fortunately, various hyperpolarization techniques are being developed to increase the sensitivity. In this talk, one of the most cost-efficient and operationally friendly, yet remarkable, approaches will be presented. This technique converts the highly-ordered nuclear spin singlet *para*-hydrogen into enhanced NMR signals (up to 10<sup>4</sup> times) through catalytic hydrogenation reactions or reversible interactions, in the presence of *para*-hydrogen, with the metal center of inorganic complexes such as Crabtree's catalyst.

For hydrogenation reactions, *in-situ* reaction monitoring using *para*-hydrogen-enhanced NMR offers dramatically increased sensitivity and unique mechanistic insights. This is because hyperpolarization with unmistakable patterns only happens in the case of pairwise addition, where the two hydrogen atoms from the same *para*-hydrogen molecule are added onto the substrate in a concerted *syn*-pathway. It is thus possible to unravel the stereoselectivity in the alkyne semi-hydrogenation reaction and provide an extraordinary window to peek at the subtle surface processes in heterogeneous catalysis. While in the non-hydrogenation mode, signal amplification by reversible exchange (SABRE) enables the detection of suitable substrates at nanomolar scale without net chemical reactions, thanks to the strong signal enhancement as a result of polarization transfer from *para*-hydrogen.

**REFERENCES**

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