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# dDNP as an emerging real time analytical method for catalytic reactions

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Dissolution dynamic nuclear polarization NMR (dDNP) hyperpolarization method is used for the investigation of enzymatic and metabolic systems. Improving the signal-to-noise ratio by more than 10.000 compared to conventional NMR, the method significantly expands the applicability and efficiency of conventional NMR[1]. We are working to develop this methodology further to include catalytic and inorganic chemistry.

The dedicated instrumentation for hyperpolarization is becoming increasingly versatile for applications within chemistry, biology and medicine and is used to answer scientific questions of a both fundamental and applied nature. By applying dDNP to catalytic science, we are allowing real time monitoring of catalytic reaction mechanisms and intermediates. Understanding the direct correlation between the structure of the catalyst and the selectivity of the reaction remains a great challenge in most of catalysis, and facilitate the continued improvement and development of new catalysts.

A target reaction of the project has been the hydrogenation of simple alkenes and alkene esters using Shrock-Osborn, Crabtree and Wilkinson's catalysts. Hydrogenation of olefins are relevant for both industrial and research applications.

We report here the results of following the hydrogenation reactions with dDNP. The suitability of various solvents and substrates, the requirements on the reaction speed and the reaction conditions have been assessed for dDNP conditions.

The potential of the method towards obtaining kinetic and mechanistic insights by time-resolved dDNP is illustrated in Figures 1 and 2. It is shown how Rh(NBD)(DPPB), a Shrock-Osborn catalyst, competitively catalyses the hydrogenation of two similar unlabeled alkene esters. The reaction has been followed with a time resolution of 2 seconds over a range of 2 minutes. It is seen how different reaction rates are observed despite equal initial substrate concentrations. The substrate with the terminal alkene reacts faster than the conjugated alkene as would be expected. The catalyst activity has been calculated from evolution of the peak intensities.

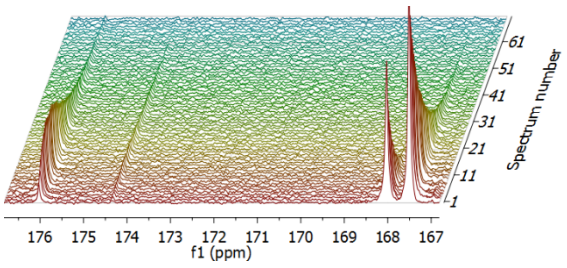


***Fig. 1*** *Hydrogenation of butyl acrylate and trans-methyl crotonate over Rh(NBD)(DPPB), a Shrock-Osborn catalyst. The stacked $^{13}$C-NMR spectra (carbonyl range of the spectra) show the time-resolved development of the system over 2 minutes. Substrate peaks are found to the right and product peaks to the left.*

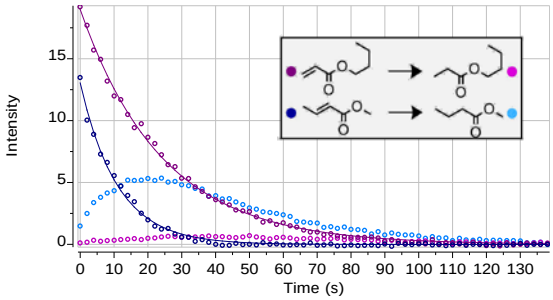


***Fig. 2*** *Time-resolved intensities of the substrate and product carbonyl peaks in Figure 1.*

Slight variations in the reaction conditions provide valuable insight into the workings of the system including substrate inhibition, rate limiting factors, kinetic isotope effects and mechanistic information. $^{13}$C-labelling substrates will potentially allow for full mechanistic elucidation and observation of intermediates.

Acknowledgments

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[1] . J. H. Ardenkjær-Larsen et al., Increase in signal-to-noise ratio of > 10,000 times in liquid-state NMR, Proc. Natl. Acad. Sci. U. S., 100, 10158–10163, 2003.