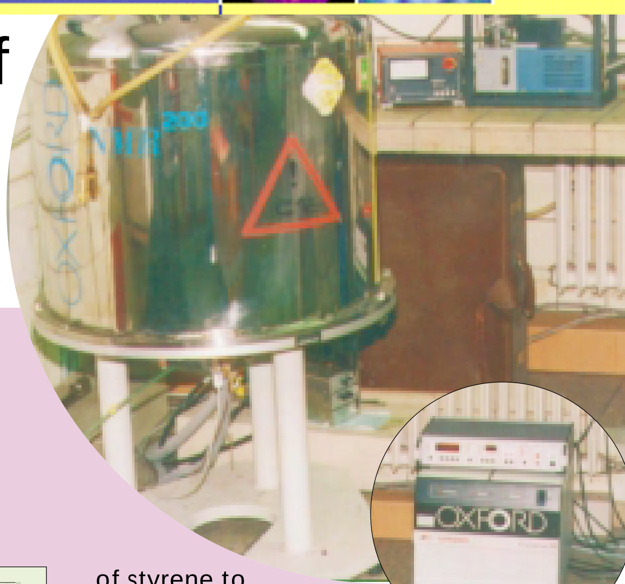
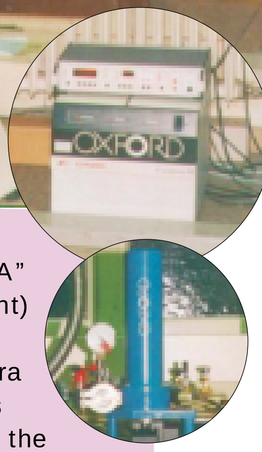
Boosting the Sensitivity of NMR Spectroscopy using Parahydrogen





The low sensitivity of NMR spectroscopy can be enhanced via Para-Hydrogen Induced Polarization (PHIP). The parahydrogen (p-H_2) is prepared by cooling H_2 to cryogenic temperatures. At liquid N_2 temperature, 52% p-H_2 is obtained. The Oxford Instruments' Closed Cycle Cooler Cryostat, however, generates virtually pure p-H_2, thereby boosting the NMR sensitivity even further.

At the University of Bonn in the Institute of Physical Chemistry, homogeneous hydrogenations mediated by organometallic catalysts are being examined in situ by Prof. Bargon and his co-workers using NMR spectroscopy in combination with parahydrogen (p-H_2). This spin isomer of dihydrogen has antiparallel nuclear spins. A significant NMR signal enhancement results from breaking the high symmetry of p-H_2 by means of a chemical reaction. This phenomenon is known either as the PASADENA effect or as PHIP (Para-Hydrogen Induced Polarization) [1,2]. The resulting proton spin polarization appears both in the final hydrogenation products and in otherwise elusive short-lived intermediates of a catalytic cycle.

The enrichment of p-H_2 achievable via cooling depends on the temperature: using liquid N_2, the fraction of p-H_2 is only ≈ 52 %. The Oxford Instruments' Closed Cycle Cooler Cryostat, together with a heat exchanger filled with charcoal as a catalyst, reaches temperatures below 20 K, and generates essentially 100%- pure p-H_2, thereby boosting the NMR enhancement even more.

The thermal conductivities of the two spin isomers of H_2 differ. Therefore, the degree of the p-H_2 enrichment is determined using two thermal conductivity cells, one filled with regular H_2, the other one with the p-H_2-enriched fraction. Together the cells form a calibrated balanced bridge (figure 1).

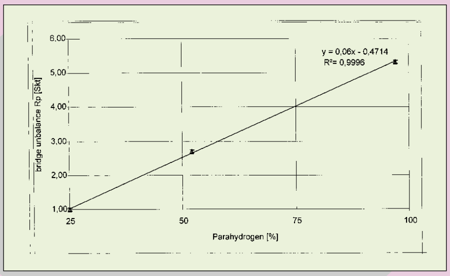


Fig. 1: Calibration of the pair of thermal conductivity cells.

Figure 2 shows the achieved level of continuous enrichment of p-H_2, which remains constant up to a flow of 20 ml/min. An operating temperature of 30 K avoids liquefaction of hydrogen, which would represent a safety risk and would also waste energy. The enriched p-H_2 is fed into the NMR sample tube through a capillary: The timing and the added amount is being controlled by the NMR pulse program.

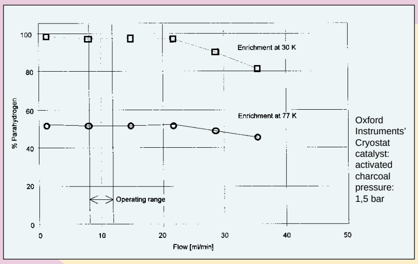


Fig. 2: Continuous flow of enriched p-H_2 using the Oxford Instruments' Cryostat.

Figure 3 shows the successful detection of a catalytic intermediate during the homogeneous hydrogenation of styrene to ethylbenzene ("ETB"): the signals labelled "PA" (for product attachment) cannot be detected in the regular NMR spectra after the reaction. This example demonstrates the attractive potential of PHIP-NMR spectroscopy. Even the kinetics of these reactions can be investigated, and thanks to the appearance of intermediates in the in situ spectra, more information is obtained than via other analytical methods.

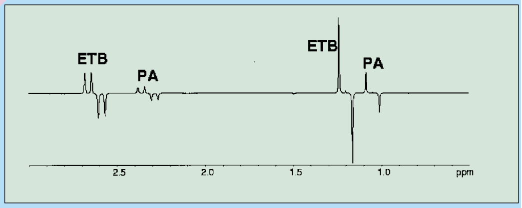


Fig. 3: In situ PHIP-NMR observation of an intermediate (PA = product attachment) when catalytically hydrogenating styrene to ethylbenzene (ETB).

References:
[1] J. Bargon in Applied Homogeneous Catalysis, B. Cornils and W. Herrmann, eds., Chapter 3.1.3, VCH, Weinheim (1996).
[2] J. Bargon, J. Kandels, H. Woelk, Z. Phys. Chem. 180 (1993) 65-93.

Contact
Dr J Bargon and Mr R Fligg,
Institute of Physical and Theoretical Chemistry, University of Bonn, Germany
E-mail: bargon@uni-bonn.de,
fligg@rsl.thch.uni-bonn.de.