

Letter

In situ PHIP NMR — a new tool to investigate hydrogenation mediated by colloidal catalysts

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Abstract

It is known that some colloidal catalysts show “homogeneous”-like behavior, but it is unclear which parameters define the borderline between heterogeneous, i.e. surface reactions, and homogeneous-type catalysis of colloidal systems. The reaction of ethynylbenzene (phenylacetylene) with parahydrogen using the colloidal palladium catalyst $\text{Pd}_x[(\text{N}(\text{octyl})_4\text{Cl})_y]$ leads to nuclear spin polarization in the hydrogenation products. Accordingly, the in situ NMR method parahydrogen induced polarization (PHIP) is an appropriate tool to investigate hydrogenation mediated by colloidal catalysts. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Parahydrogen induced polarization (PHIP) [1–4] is a well known in situ NMR method, which has been used extensively [5,6] as an effective tool for the investigation of homogeneously catalyzed hydrogenation. Using parahydrogen ($p\text{-H}_2$), in situ recorded ^1H NMR spectra show spin polarization due to the breakdown of the high symmetry of the $p\text{-H}_2$ molecule. These characteristic PHIP patterns are observed only if the transfer of the two parahydrogen atoms occurs in a pair-wise manner, i.e. simultaneously, whereby the transferred protons have to experience some sort of mutual magnetic coupling at any time. The spin polarization of the hydrogenated molecules leads to

signal enhancements of up to 10^4 [1,2]. Therefore, it is not only possible to detect final hydrogenation products at very low concentrations, but also catalytic intermediates like transition metal dihydrides or catalyst–substrate complexes can be observed. The polarization patterns reveal information about the mechanism and the kinetics of the reaction and the structure and the mode of formation of the polarized products.

Heterogeneous catalysts are not expected to give rise to the PHIP effect, since the spin correlation in the adsorbed $p\text{-H}_2$ is considered to be lost once the dihydrogen molecules interact with a catalytically active surface. Therefore, the most likely hydrogen atoms transferred in such a fashion would stem from different $p\text{-H}_2$ molecules. However, we have shown that the colloidal transition metal catalyst used gives rise to the PHIP phenomenon, thereby implying a homogeneous reaction pathway and proving that the two

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transferred hydrogen atoms stem from the same dihydrogen molecule.

2. Experimental

Five millimeter NMR tubes were charged with 100 μl ethynylbenzene, 6 mg of the catalyst $\text{Pd}_x[(\text{N}(\text{octyl})_4\text{Cl}]_y$, and 0.7 ml of acetone- d_6 and placed into a 200 MHz spectrometer. Fifty percent-enriched $p\text{-H}_2$ was prepared via catalytic equilibration over charcoal at 77 K [5] and injected repeatedly in synchronization with the pulsed NMR experiment via an electromechanically lowered glass capillary mechanism. Higher levels of $p\text{-H}_2$ enrichment, namely >97% have also been achieved using a closed cycle cooler cryostat [7].

Fig. 1 shows PHIP-NMR spectra obtained during the hydrogenation of ethynylbenzene with $p\text{-H}_2$. In order to eliminate interfering signals originating from spins in thermal equilibrium, i.e. ‘non-PHIP signals’, the NMR spectra were acquired after a hydrogenation time of 10 s accumulating the responses to different pulse angles [8]. The maximum signal intensity for PHIP signals occurs at a flip angle of 45° , in contrast to the usual ‘ 90° pulse’ used for substrates in thermal equilibrium. Therefore, by alternately adding and subtracting scans acquired using pulse angles of -45° and 135° , respectively, it is possible to minimize or even suppress the signal intensity of the unpolarized, the so-called ‘thermal’ proton spins, whereas the signals of the proton spins in polarization then display the maximum of their signal intensity [8]. Less than

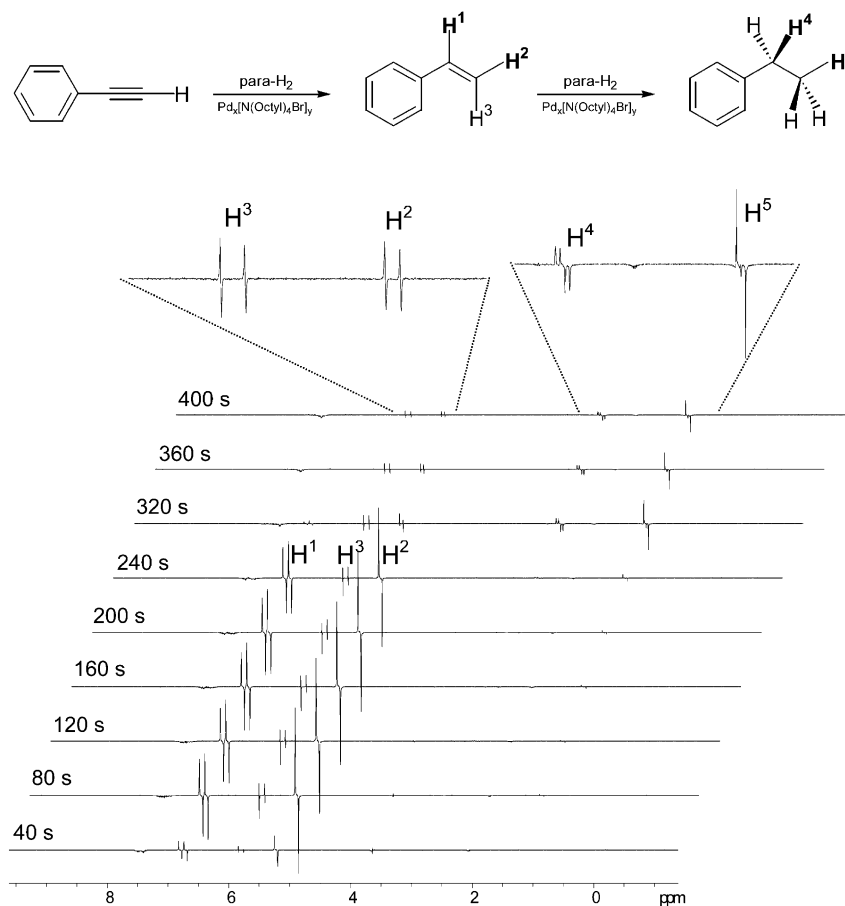


Fig. 1.

perfect elimination of the thermal signals may occur, nevertheless, in part because of a slight drift of the external magnetic field (B_0), or because of changes of the homogeneity.

Each spectrum shown in Fig. 1 is the result of four accumulated scans and 40 s of hydrogenation time each.

3. Results and discussion

Hydrogenation of ethynylbenzene to the Z-product leads to polarization signals in the respective positions H^1 and H^2 of styrene, as is detected. Furthermore, polarization also occurs in position H^3 . This signal shows an anti-phase coupling of 1 Hz with its geminal hydrogen. Whether this is a result of geminal transfer of *p*- H_2 parahydrogen to the positions H^2 and H^3 , or the consequence of a nuclear Overhauser effect, will soon be discriminated using deuterated ethynylbenzene.

With proceeding hydrogenation the concentration of ethynylbenzene decreases; therefore, the positions H^1 and H^2 show less and less polarization. Subsequently, the polarization signals H^4 and H^5 of ethylbenzene, the hydrogenation product of styrene, appear. Accordingly, ethylbenzene is formed via homogeneous catalysis as well, i.e. two more *p*- H_2 protons are transferred simultaneously.

4. Conclusions

The hydrogenation of ethynylbenzene to styrene as well as that of styrene to ethylbenzene mediated by

the colloidal catalyst $Pd_x[(N(octyl)_4Cl)_y]$ occurs in a “pair-wise” fashion, i.e. the two hydrogen atoms of dihydrogen are transferred simultaneously, which is characteristic of a homogeneous hydrogenation. This in situ NMR experiment convincingly demonstrates the unique power of PHIP for the investigation of hydrogenation mediated by colloidal systems. Additional in situ NMR experiments will be conducted to investigate if more features of homogeneous catalysts apply to colloidal systems as well.

References

- [1] C.R. Bowers, D.P. Weitekamp, Phys. Rev. Lett. 57 (1986) 2645–2648.
- [2] C.R. Bowers, D.P. Weitekamp, J. Am. Chem. Soc. 109 (1987) 5541–5542.
- [3] T.C. Eisenschmid, R.U. Kirss, P.P. Deutsch, S.I. Hommeltoft, R. Eisenberg, J. Bargon, R.G. Lawler, A.L. Balch, J. Am. Chem. Soc. 109 (1987) 8080–8091.
- [4] J. Bargon, J. Kandels, K. Woelk, Z. Phys. Chem. 180 (1993) 65–93.
- [5] J. Bargon, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, VCH: Weinheim, 1996, Vol. II, p. 672.
- [6] S.B. Duckett, C.J. Sleight, Prog. Nucl. Magn. Reson. Spectrosc. 34 (1999) 71–92.
- [7] J. Bargon, R. Fligg, Oxford Research Matters, Vol. 12, 2000.
- [8] J. Natterer, J. Bargon, Prog. Nucl. Magn. Reson. Spectrosc. 31 (1997) 293–315.