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Bridging the Gap: From Homogeneous to Heterogeneous Parahydrogen-induced Hyperpolarization and Beyond

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In memoriam Kirill V. Kovtunov

Demonstration of parahydrogen-induced polarization effects in hydrogenations catalyzed by heterogeneous catalysts instead of metal complexes in a homogeneous solution has opened an entirely new dimension for parahydrogen-based research, demonstrating its applicability not only for the production of catalyst-free hyperpolarized liquids and gases and long-lived non-equilibrium spin states for potential biomedical applications, but also for addressing challenges of modern fundamental and industrial catalysis including advanced mechanistic studies of catalytic reactions and operando NMR and MRI of reactors. This essay summarizes the progress achieved in this field by highlighting the research contributed to it by our colleague and friend Kirill V. Kovtunov whose scientific career ended unexpectedly and tragically at the age of 37. His role in this research was certainly crucial, further enhanced by a vast network of his contacts and collaborations at the national and international level.

It is a curious coincidence that parahydrogen-induced polarization (PHIP) effects were reported[1] – albeit not yet recognized as such and interpreted as chemically induced dynamic nuclear polarization (CIDNP) – in 1983, the same year that Kirill Kovtunov (Figure 1) was born. The true meaning of the 1983 observations of Bryndza et al. became clear after the publication of the work of Bowers and Weitekamp[2,3] in 1986–1987. They demonstrated, first theoretically and then experimentally, that if parahydrogen is used in the hydrogenation of acrylonitrile to propionitrile in a solution of Wilkinson's organometallic catalyst, this results in the enhancement of NMR signals. Since then, the field of PHIP has grown tremendously,[4,5] and a number of remarkable developments of this hyperpolarization technique have emerged over the last 10 years or so, including PHIP by side-arm hydrogenation (PHIP-SAH),[6] signal amplification by reversible exchange (SABRE),[7] SABRE-RELAY,[8] etc.

Nowadays, parahydrogen-based research is mostly driven by the incentive to develop novel contrast agents for biomedical MRI and MRS.[9,10] There is, however, another point of entry to the field of PHIP – through chemical engineering

Figure 1. Kirill V. Kovtunov (14. 01. 1983–19. 05. 2020) was born in Barnaul, the Altai region of Russia. In 2000–2005 he was a student at the Novosibirsk State University. After graduation in 2005, he joined the MR microimaging laboratory at ITC SB RAS as a PhD student. He defended his PhD thesis entitled "Parahydrogen-induced polarization of nuclear spins in heterogeneous catalytic hydrogenation reactions" on June 18, 2008. After that, he continued to explore this research field further, and defended his Habilitation thesis entitled "Parahydrogen-induced NMR signal enhancement in heterogeneous catalysis" on December 25, 2019.

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An invited contribution to a Special Collection on Parahydrogen Enhanced Resonance

and catalysis. Already in the first publications on the subject[3,11] it was recognized that PHIP can be observed not only for the reaction products but also for the short-lived intermediates such as metal dihydride complexes, thereby holding the potential to unveil the underlying sophistication of reaction mechanisms. This has been explored later in the context of H_2 activation by transition metal complexes in solution.[12]

During his undergraduate studies at Novosibirsk State University (NSU), Kirill was involved in the pulsed-field-gradient NMR and MRI studies of gas and liquid transport in various geometries including porous media and microreactors at the NMR microimaging group at ITC. Other research that was done by group members included operando studies of catalytic processes, with a setup designed to place a single catalyst pellet or a catalyst bed in the probe of a microimaging instrument to study dynamic redistribution of the liquid phase in the catalyst and performing MR imaging and spatially resolved NMR spectroscopy of the reaction progress.[13] Heterogeneous hydrogenations, which are widely used in industrial catalysis, were of primary interest in those studies, and not surprisingly, the idea to use parahydrogen in these processes was being entertained for some time. After graduating from NSU in 2005, Kirill joined the group at ITC as a PhD student. From then on, his research was about combining magnetic resonance, catalysis, and parahydrogen.

The main objective for his PhD thesis was to demonstrate PHIP in heterogeneous hydrogenations, even though it has been pronounced impossible earlier in the literature.[14] The solution to this "impossible" problem was sought via the known bridge between homogeneous and heterogeneous catalysis, namely by immobilizing PHIP-active organometallic complexes on a suitable solid support. Despite its deceptive conceptual simplicity, this approach has proven difficult to implement. Many unsuccessful attempts to immobilize various Rh and Ir metal complexes and use them in PHIP experiments resulted in no catalytic activity, or no PHIP effects, or metal complex leaching into solution, or all of the above. The breakthrough came in the end of 2006 when Kirill was visiting the Department of Chemistry at UC Berkeley within the framework of a joint project of the CRDF cooperative grants program implemented by the ITC microimaging team and the group of Alex Pines.

The first successful experiments (Figure 2a) were performed initially with the hydrogenation of styrene in solution using Wilkinson's catalyst immobilized on silica or a polymer.[15] In these experiments, clear PASADENA (PArahydrogen and Synthesis Allow Dramatically Enhanced Nuclear Alignment)[3] effects were observed for the reaction product ethylbenzene. Importantly, essentially no PHIP effects were detected once the catalyst was removed from the slurry, which is very easy to achieve with these solid materials. While these first successful observations were encouraging, they were not completely unambiguous. A more clear-cut proof was thus sought that PHIP effects were observed in a heterogeneous reaction and not as a result of metal complex leaching. This was achieved as well, based on the hydrogenation of propylene into propane over silica-immobilized cationic Rh complex or Wilkinson's catalyst (Figure 2b). Leaching of the metal complex is not possible in such gas-solid hydrogenation processes performed in the absence of any liquid phase. Successful demonstration of both PASADENA and ALTADENA (Adiabatic Longitudinal Transport After Dissociation Engenders Nuclear Alignment)[16] effects in those experiments provided an ultimate proof that those experiments indeed resulted in the first demonstration of PHIP in heterogeneous catalysis (HET-PHIP).

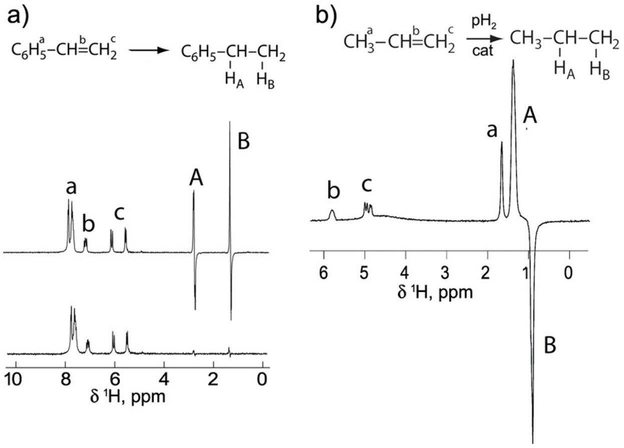

Figure 2. a) ${}^1H$ NMR spectra acquired after bubbling parahydrogen through the C_6D_6 solution of styrene at 7 T in the presence of polymer-supported Wilkinson's catalyst (top) or after catalyst removal (bottom). b) ${}^1H$ NMR spectrum acquired during gas-solid hydrogenation of propylene with parahydrogen over silica-supported Wilkinson's catalyst in the Earth's magnetic field. Adapted with permission from Ref. [15] Copyright (2007) American Chemical Society.

Coincidentally, this happened at the same location (Department of Chemistry, UC Berkeley) where 23 years earlier homogeneous PHIP effects were observed for the first time.

The PHIP studies with immobilized metal complexes continue, and by now many other examples have been demonstrated, for instance the cationic Au complex immobilized on a metal-organic framework (MOF).[17] Immobilized metal complexes certainly represent a useful model system which can provide a useful bridge between homogeneous and heterogeneous hydrogenations with parahydrogen and can help in advancing our understanding of HET-PHIP in general.

At the same time, such immobilized metal complexes are not very stable, particularly at high temperatures and in the presence of reducing agents such as H_2, and thus are not used in industrial applications. Instead, much more robust catalysts such as supported metal NPs are preferred for such reactions. However, supported and bulk metals were not expected to be able to achieve pairwise H_2 addition to an unsaturated substrate, which is a major prerequisite for efficient PHIP production. Indeed, H_2 chemisorption on metals is very efficient but dissociative, and hydrogen atoms are known to be extremely mobile on the metal surface. Therefore, hydrogenation would be expected to inevitably involve random H atoms, making pairwise addition of H_2 impossible. But Kirill was not quite convinced by this common knowledge, and in less than a year demonstrated both PASADENA- and ALTADENAtype effects in hydrogenation of propylene to propane over supported Pt and Pd NPs.[18] Remarkably, for the very first such experiments he accidentally used a Pd/Al_2O_3 catalyst which was heavily doped with Mn^{2+} for performing rapid MRI experiments of hydrogenations and was certainly not intended for parahydrogen studies. Luckily, this experiment worked despite the paramagnetic doping of the catalyst. Later studies also confirmed that magnetic nature of a catalyst is not necessarily an obstacle for observing PHIP effects, as demonstrated, for instance for the catalyst comprising superparamagnetic Co nanoparticles on TiO_2 support.[19]

Observation of PHIP effects with supported metal NPs contradicted the commonly accepted Horiuti-Polanyi mechanism of hydrogenation by metals and required some explanation. The one advanced originally was based on the fact that under realistic conditions the surface of a catalytically active metal is never clean during the reaction; it is covered with various species and is thus possibly partitioned into smaller clean patches of metal so that the reactants are forced to stay together. This may prevent H atoms from separating freely on the catalyst surface. However, this explanation has never been experimentally tested, and recent results show that it may be incorrect.[19,20]

Based on these innovative and exciting results, Kirill defended his PhD thesis in 2008 with flying colors. But the work certainly didn't stop there. The scope of HET-PHIP has been growing ever since, covering all sorts of different catalysts, which now include various bulk and supported metals (Pt, Pd, Rh, Ir, Au, Ag, Co, Cu), metal oxides (Cr_2O_3, CeO_2, CaO, TiO_2),[21] carbides (Mo_2C)[22] and sulfides (MoS_2),[23] different particle sizes, various solid supports, substrates, conditions, etc.[19,20] One example is shown in Figure 3 for hydrogenation of propyne over supported Cu NPs, demonstrating pronounced PHIP effects.[24] It is also observed that introduction of a phosphine ligand to the Cu NPs decreases the catalytic activity markedly but at the same time NMR signal enhancements become larger. Observation of HET-PHIP effects with Mo sulfide catalysts[23] made it possible to study thiophene hydrodesulfurization reaction, which is a model for industrial purification of fuels. Other industrially important processes can certainly be addressed and their mechanisms and kinetics studied.

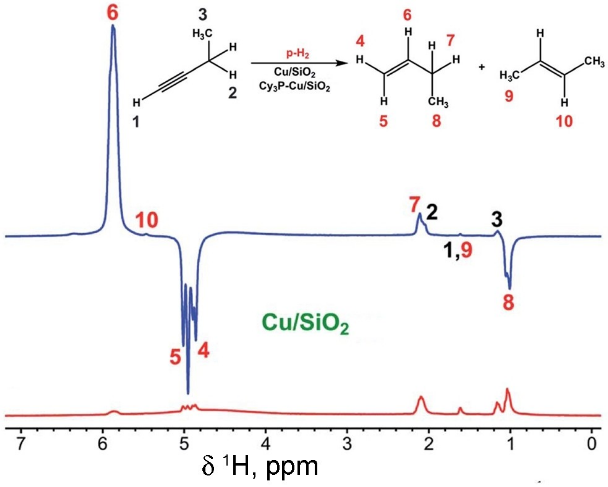

Figure 3. The reaction scheme of 1-butyne hydrogenation over Cu/SiO_2 catalysts, and the ^{1}H NMR spectra acquired during the reaction while the gas was flowing (top) and after rapid interruption of the gas flow and subsequent relaxation of nuclear spins to thermal equilibrium (bottom). Adapted from Ref. [24] published by The Royal Society of Chemistry in accordance with the term of the CC-BY 3.0 licence. Copyright (2017) The Authors.

From the very beginning, a lot of PHIP work was performed with gases with their rather short polarization lifetimes, usually below 1 s for hydrocarbon gases at normal pressures. Many efforts were thus directed at extending these lifetimes, particularly by exploring the properties of long-lived spin states (LLSS) at low magnetic fields[25,26] and also by condensing hyperpolarized (HP) gases into a liquid state or dissolving them in liquids,[27] with up to tens of seconds of HP lifetime achieved this way. Also, alternative ways were explored to produce HP propane, for instance by hydrogenating cyclopropane with parahydrogen.[28] One very recent example of HET-PHIP with gases is the production of HP diethylether,[29,30] an inhalable anesthetic, by hydrogenation of an unsaturated precursor in the liquid or in the gas phase, as well as exploring its LLSS in a low magnetic field. HET-PHIP was also successfully used to enhance MR imaging experiments, for instance to address gas flow in various geometries (Figure 4), and to obtain 2D and 3D maps of product distribution in a model catalytic reactor.[31]

While supported metals do work in PHIP experiments, at present the achieved polarizations normally do not exceed a few percent in experiments where significant product yields have been achieved. Therefore, an active search for better heterogeneous catalysts continues. One of the current trends is to explore the so-called single-atom and single site heterogeneous catalysts.[32,33] This can be exemplified by intermetallic Pd–In NPs supported on Al_2O_3.[34] In this system, individual Pd atoms are essentially surrounded by inactive In atoms, providing a single metal atom configuration of the active catalytic center. And indeed, this catalyst provides substantial polarization levels and reaction yields and is able to enhance the NMR signals significantly, thus facilitating the MR imaging of gases (Figure 5).

The scope of the research Kirill was involved in is very broad. Exploring the concept of PHIP-SAH introduced by Silvio Aime,[6,35,36] which involves hydrogenation of unsaturated precursors followed by hyperpolarization transfer to ^{13}C nuclei, is exemplified by the efforts to produce catalyst-free HP liquids or solutions by hydrogenation of a substrate vapor and its subsequent dissolution and hydrolysis, for instance, to yield HP ethanol in solution which never contained any catalyst.[37] In the context of potential biomedical applications, aqueous hydrogenations are very important and are being addressed.[38] Other remarkable achievements include the demonstration of the unexpected spontaneous SABRE in high magnetic fields[39] and observation of HET-SABRE with an Ir complex immobilized on a solid material.[40] Another approach is to perform SABRE in a traditional way in solution with subsequent removal of the dissolved metal complex with a thiol-functionalized porous solid material to produce a clear catalyst-free HP solution.[41]

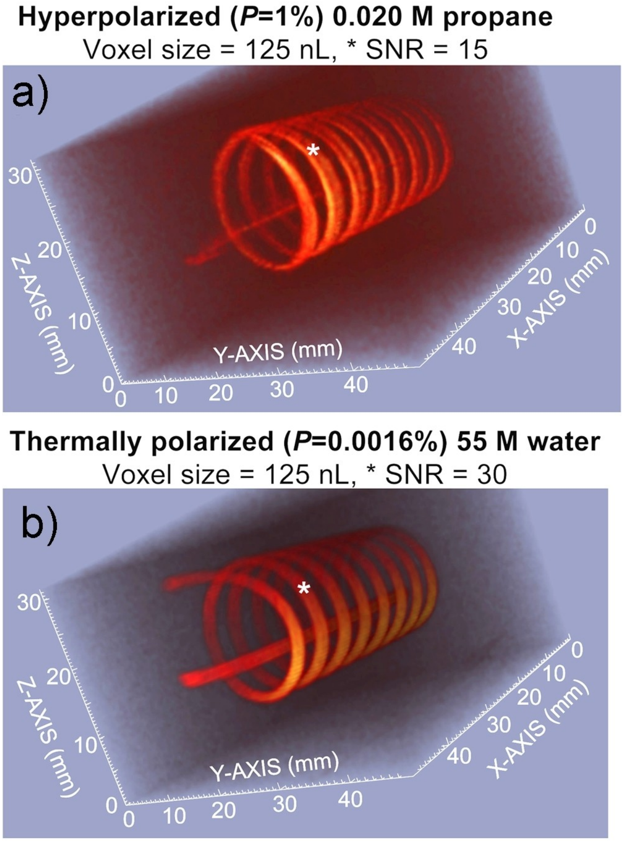

Figure 4. 3D gradient echo MRI of a spiral tube with continuously flowing HP propane (a) and static water (b) acquired with 0.5 mm isotropic spatial voxel resolution in 21.4 s at 4.7 T. A comparable SNR is obtained despite the dramatic difference in gas and liquid spin densities. Adapted with permission from Ref. [25]. Copyright (2014) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

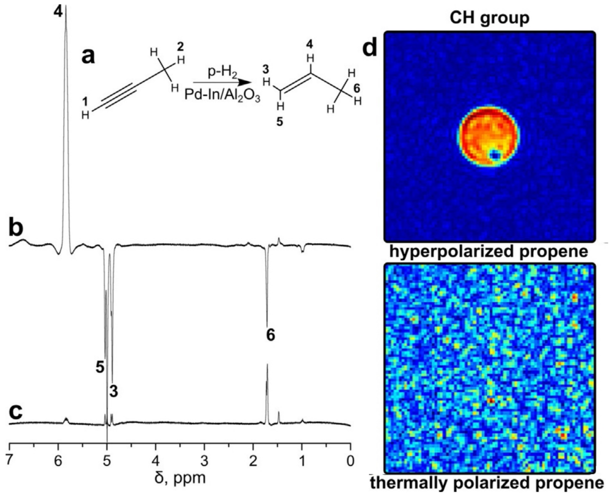

Figure 5. a) The reaction scheme for propyne hydrogenation over Pd–In/Al_2O_3 catalyst. b) and c) ^1H NMR spectra acquired during the reaction (b) while the gas was flowing and (c) after an abrupt interruption of the gas flow and the subsequent relaxation of nuclear spins to thermal equilibrium. (d) MR images of a 10 mm NMR tube filled with propylene in thermal equilibrium (bottom) or hyperpolarized propylene (top). Adapted with permission from Ref. [34]. Copyright (2018) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Some notable work has been done on polarization transfer to ^{15}N nuclei to extend hyperpolarization lifetimes to many minutes.[42–44] For instance, SABRE of nitrogen-containing drugs is exemplified by HP fampridine which made it possible to perform ^{15}N MRI at natural abundance of the ^{15}N isotope.[45]

The joint CRDF project mentioned earlier, in addition to its successfully achieved primary objective of demonstrating HET-PHIP effects, encompassed numerous other objectives which were rather challenging and ambitious. One of those was about the use of ultralow field NMR to monitor catalytic processes in metal containers. It has been finally achieved this year, in collaboration between the Novosibirsk team and the group of Prof. D. Budker at Helmholtz Institute in Mainz. In that study,[46] unsaturated acetylenic compound was hydrogenated with parahydrogen in a metal tube and the NMR spectra were detected with an atomic magnetometer at zero magnetic field, demonstrating that such approach is indeed promising for studying heterogeneous systems and for applications in heterogeneous catalysis. This was one of the last studies in which Kirill was involved.

For many years now, one of the incentives was to think outside the box and go beyond parahydrogen, and in particular to introduce the use of nuclear spin isomers of molecules (NSIM) other than H_2 and D_2 for nuclear spin hyperpolarization. One remarkable example is the successful chemical enrichment of NSIM of ethylene by hydrogenation of acetylene with parahydrogen.[47] Ethylene is a symmetric molecule, so to demonstrate the NSIM enrichment of ethylene, a further reaction is required to break its symmetry by producing a non-symmetric product. And indeed, in such an experiment the PHIP effects were clearly observable for the non-symmetric product, proving that enrichment of NSIM of ethylene does take place in acetylene hydrogenation with parahydrogen. While a more direct experiment to confirm chemical synthesis of NSIM would be a plus,[48] these preliminary results provide a clear glimpse into the bright and promising future of NSIM-based hyperpolarization. Notably, NSIM of ethylene is also a remarkable example of the molecular long-lived spin states (LLSS), which are becoming increasingly popular for achieving spin hyperpolarization storage times (T_{LLSS}) that significantly exceed the conventional spin relaxation times (e.g., T_1).[49] In particular, transferring the singlet spin state of a p-H_2 molecule to a reaction product is a natural way of producing such states, and the chemical NSIM enrichment of ethylene convincingly demonstrates such a possibility – the ratio $T_{LLSS}/T_1 \sim 3500$ measured for ethylene is likely the largest value reported so far for any molecule except p-H_2 itself.

While a lot has been already achieved in bridging the gap between utilizing parahydrogen in homogeneous and heterogeneous processes, this is clearly just the tip of an iceberg. Further progress in this field requires a much deeper understanding of the processes involved, particularly for nanoparticle-based catalysts, and further optimization of catalysts and reaction conditions to implement these processes with maximum possible efficiency. The extent of knowledge accumulated to date is already adequate for developing mechanistic models that are sufficiently realistic to guide further research and applications in this field. In particular, as revealed by previous studies, one clear possibility to improve the PHIP efficiency of heterogeneous catalysts is a broader exploration of single-site and single-atom catalyst structures. This parallels the recent trend in fundamental catalysis, and can thus potentially spearhead future research and applications toward multiple goals, from producing highly polarized catalyst-free fluids for advanced spectroscopic and imaging studies to exploring the mechanistic details of important catalytic transformations. Future advances in these directions will be the best possible tribute to the efforts of Kirill Kovtunov to launch and promote this field of research.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: parahydrogen-induced hyperpolarization · NMR signal enhancement · heterogeneous hydrogenation · immobilized metal complexes · supported metal catalysts

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