Polarization Transfer Efficiency in PHIP Experiments

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Supporting Information

1) Derivation of equation (3)

In thermal equilibrium at room temperature the singlet state $|S_0\rangle$ and the three triplet $|T_+\rangle$, $|T_0\rangle$, $|T_-\rangle$ of hydrogen are nearly equally populated ($x_{|S_0\rangle} = x_{|T_+\rangle} = x_{|T_0\rangle} = x_{|T_-\rangle} = 0.25$). The singlet state represents \textit{para}hydrogen, \textit{ortho}hydrogen is represented by the triplet states. It follows that the net fraction of \textit{ortho}hydrogen $x_{\text{ortho}}$ equals three times the fraction of \textit{para}hydrogen $x_{\text{para}}$ ($x_{\text{ortho}} = 3 x_{\text{para}}$ or $x_{\text{para}} = x_{\text{ortho}}/3$). The fraction of \textit{para}hydrogen leads to hyperpolarization. In order to calculate the hyperpolarized fraction $x_{hp}$ of \textit{para}-enriched hydrogen, the fraction of \textit{para}hydrogen that would be present in thermal equilibrium ($x_{\text{para}} = x_{\text{ortho}}/3$) has to be subtracted from the total fraction of \textit{para}hydrogen:

$$x_{hp} = x_{\text{para}} - \frac{x_{\text{ortho}}}{3}$$

With $x_{\text{para}} + x_{\text{ortho}} = 1$ the fraction of hyperpolarized hydrogen is as follows:

$$x_{hp} = x_{\text{para}} - \frac{1 - x_{\text{para}}}{3}$$

2) Determination of the PTE

In the following the processing procedure is presented in detail for one experiment (c(RhBINAP)=0.1 mM), all others were processed accordingly. The hydrogenation reaction was recorded by applying consecutive 45 degree pulses. Figure S1a shows a spectrum at the beginning of the hydrogenation with \textit{para} enriched H\textsubscript{2}. In order to determine the time dependent function $n_{tot}(t)$ (Step 1, Eq. 1) either the time course of the intensity of a product or educt peak was determined. We chose peak C arising from the CH\textsubscript{2}-group of the product butyl propionate (Fig. S1a) as this group is not hyperpolarized by $p$-H\textsubscript{2}. Peak A and B of the product are not suitable, because the signal intensities are not directly proportional to the amount of substances due to hyperpolarization.
The time course of Peak C is shown in Figure S1b and the corresponding signal intensities are presented in Figure S2a. As the total molar amount of the substrate is known, the peak intensities can be converted to the molar amount of the product (Fig. S2b). $n_{tot}(t)$ is determined by a data fit (red line, Fig. S2b), the resulting kinetic parameters for all samples are summarized in Table S1. Once $n_{tot}(t)$ is known the hydrogenated amount per interval $\Delta n(t)$ (Eq. 2) can be calculated. The time course of $\Delta n(t)$ is shown in Fig. S2b. In contrast to $n_{tot}(t)$, $\Delta n(t)$ decreases with time as the hydrogen amount depletes with time.

The next step is the determination of the ideal amount $n_{P^*,i}(t)$ of $P^*$ at the end of each time interval and of the experimental obtained value $n_{P^*,\text{exp}}(t)$. As $\Delta t$ is known and $k_{hyd}$ as well as $T_1$ are determined, $n_{P^*,i}(t)$ is simply calculated by Eq. 4. The determination of $n_{P^*,\text{exp}}(t)$ includes the analysis of the quartet
of the methylene group. The spectral structure of the methylene quartet changes as a function of the reaction time (Fig. S3a). In the beginning of the hydrogenation the HP fraction is dominating and the relative line intensities are close to 1:1:-1:-1. As hydrogen amount depletes, the line intensities approach 1:3:3:1. In order to quantify the fraction of thermal and hyperpolarization, we first determine the ratio \( r_{12} \) of the intensity of peak 1 to peak 2 (Fig. S3b). The fraction of thermal (\( x_{s,tp} \)) and hyperpolarization (\( x_{s,hp} \)) is calculated with \( x_{s,hp} + x_{s,tp} = 1 \) and Eq. 6. As shown in Fig. S3c \( x_{s,hp} \) decreases and \( x_{s,tp} \) increases with time.

![Figure S3. a) Time courses of the peaks (p1-p4) deriving from Signal B (Fig. S1a). b) Time course ratio \( r_{12} \). c) Signal fraction of hyperpolarization (red) and thermal polarization.](image)

Once the total amount of product \( n_{\text{tot}}(t) \) as well as signal fractions \( x_{s,hp} \) and \( x_{s,tp} \) are known, the number of hyperpolarized product \( n_{P^*,\text{exp}} \) can be determined. From Equation 5 we follow that the ratio of \( n_{P^*,\text{exp}} \) and \( n_{P,\text{exp}} \) is:

\[
\frac{n_{P^*,\text{exp}}(t)}{n_{P,\text{exp}}(t)} = \frac{x_{s,hp}(t) P_{tp}}{x_{s,tp}(t) P_{hp}}
\]

(Rearranging Eq. S1 leads to:

\[
n_{P^*,\text{exp}}(t) = \frac{x_{s,hp}(t) P_{tp}}{x_{s,tp}(t) P_{hp}} n_{P,\text{exp}}(t)
\]

(S2)

\[
n_{P,\text{exp}}(t) = \frac{x_{s,tp}(t) P_{hp}}{x_{s,hp}(t) P_{tp}} n_{P^*,\text{exp}}(t)
\]

(S3)

By merging Eq. S3 into \( n_{\text{tot}}(t) = n_{P^*,\text{exp}}(t) + n_{P,\text{exp}}(t) \), we get:

\[
n_{\text{tot}}(t) = n_{P^*,\text{exp}}(t) + \frac{x_{s,tp}(t) P_{hp}}{x_{s,hp}(t) P_{tp}} n_{P^*,\text{exp}}(t)
\]

(Rearranging Eq. S4 leads to Eq. 7 in the main text. The thermal polarization at 14.09 T is \( P_{\text{hp,14T}} = 4.9 \cdot 10^{-5} \) and at 7.05 T we get \( P_{\text{hp,7T}} = 2.4 \cdot 10^{-5} \). The time courses of \( n_{P^*,i} \) and \( n_{P^*,\text{exp}} \) are shown in (Fig S4a). The PTE determined by using Eq. 8 is plotted vs. time in Fig. S4b.)

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3) \( \text{o-H}_2 \) NMR signal intensities

Figure S5 shows the NMR signal intensities for \( \text{o-H}_2 \) for the hydrogenation reaction with \([\text{Rh(COD)BINAP}]\text{BF}_4 (c = 0.05 \text{ mM})\) and \([\text{Rh(COD)DPPB}]\text{BF}_4 (c = 0.01 \text{ mM})\). The initial hydrogen amount, the \text{para} fraction as well as the effective hydrogenation rate constant \( k_{\text{hyd}} \) is similar for both samples (Table S1). That means that the total molar amount of \( \text{H}_2 \) will be approximately the same for the time course. At the beginning, \( I_{\text{H}_2} \) is nearly the same for both samples, during the time course, \( I_{\text{H}_2} \) for DPPB stays almost constant, where \( I_{\text{H}_2} \) for BINAP decreases linearly. A higher \( \text{H}_2 \) signal with same molar amount of \( \text{H}_2 \) must be connected to a higher \( \text{o-H}_2 \) fraction.

Figure S5: \( \text{o-H}_2 \) NMR signal intensities for the hydrogenation reaction with \([\text{Rh(COD)BINAP}]\text{BF}_4 (c = 0.05 \text{ mM})\) and \([\text{Rh(COD)DPPB}]\text{BF}_4 (c = 0.01 \text{ mM})\).