

Orthodeuterium Induced 1H- and 2D-Hyperpolarization for MRI

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Introduction

Dramatically enhanced signals occur in ²H-NMR spectra, if ortho-enriched deuterium (o-D₂) is used for *in situ* hydrogenations. Similar to Parahydrogen Induced Polarization (PHIP), but quite different in detail, Orthodeuterium Induced Polarization (ODIP) yields hyperpolarized molecules with unique features. The systems investigated yield strong polarization of the original o-D₂ nuclei, however, other magnetically active heteronuclei of the reaction product including ¹H and ¹³C exhibit polarization as well, especially if the reactions are carried out at very low magnetic field. Whereas the spin-lattice relaxation times (T₁) of the polarized deuterons are relatively short due to their quadrupole moments, polarized protons or heteronuclei in the hydrogenation products benefit from the lower magnetic moment of the deuterons. Consequently, the T₁ of protons are longer in case of ODIP than in the corresponding PHIP situation.

Results

When hydrogenating methyl propiolate or phenylacetylene in the presence of the catalyst [Rh(cod)(dppb)]BF₄ with o-D₂ prepared electrolytically from D₂O and enriched to 75% at 30 K in our regular PHIP apparatus, the products as shown in Figure 1 were obtained. Their T₁-times determined in acetone-d₆ are indicated. The *enhancement factor* for ¹H in the hydrogenation with o-D₂ of methyl propiolate using the catalyst [Rh(cod)(dppb)]BF₄ is > 100.

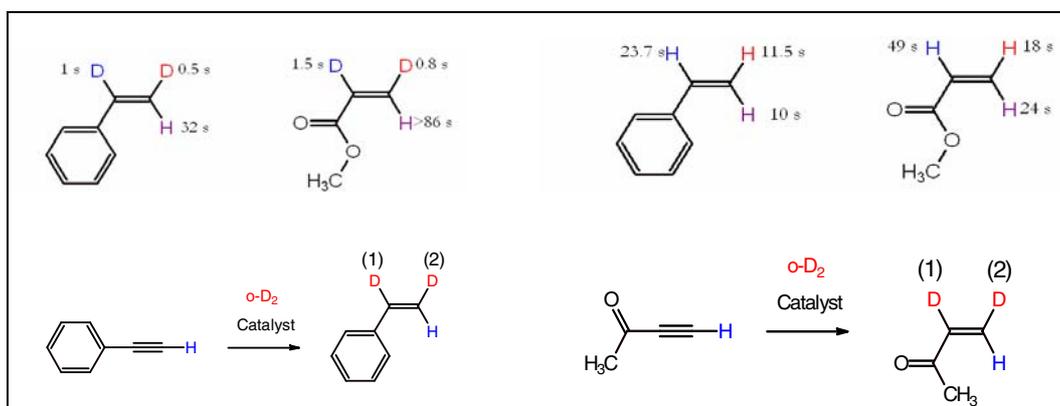


Figure 1: The reactions and products examined using enriched o-D₂ and their T₁ - relaxation times

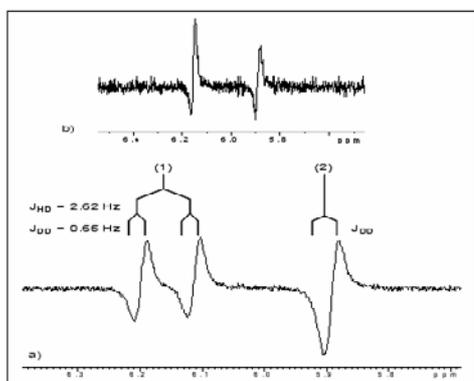


Figure 2

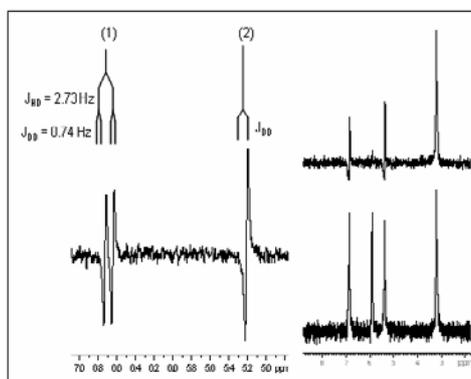


Figure 3

Figure 2: a) ODIP spectrum recorded during the reaction of methyl propiolate with o-D₂ to methyl acrylate-d₂ (o-D₂ enriched at 30 K). b) Same as a) but with ¹H decoupling (o-D₂ enriched at 77 K).

Figure 3: *Left side:* spectrum of polarized phenyl-acetylene-d₂. *Right side:* spectrum of polarized phenylacetylene-d₃ and the product spectrum recorded at thermal equilibrium.

Discussion and Conclusions

Despite the lower achievable o-D₂ enrichment as compared to p-H₂ and the short T₁ of the deuterium nuclei due to their quadrupole moment, the ¹H nuclei in the partially deuterated hyperpolarized molecules have long T₁ (> 1 minute), which makes them attractive as ¹H-hyperpolarized contrast agents for ¹H-MRI investigations. Likewise, ¹³C- or ¹⁵N- hyperpolarized molecules with longer T₁-times and different polarization patterns can be provided in this fashion.