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NMR-DETECTION OF INTERMEDIATES DURING HOMOGENEOUS HYDROGENATION OF DIENES USING PARAHYDROGEN

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Summary: 1. The ^{1}H-NMR spectra of the reaction products of hydrogenations using parahydrogen reveal information about intermediates and thus the reaction mechanism. 2. Due to its high signal enhancement the method is uniquely suited for reactions, where the catalyst itself becomes chemically modified.

As has been shown before, oxidative addition and homogeneous hydrogenation with either para- or ortho-enriched hydrogen yield strong nuclear spin polarization in the NMR spectra of the reaction products.[1–9] In this communication we want to demonstrate that the polarization pattern in the reaction product reveals information about the reaction path. This allows to characterize intermediates, a type of information, which is otherwise difficult to obtain. Furthermore, due to the high signal enhancement, this method has a high sensitivity for minor reaction products, and is, therefore, very well suited to investigate *in situ* such reactions, where the catalyst itself becomes hydrogenated. Thereby nuclear spin polarization is observed, even if the hydrogen atoms derived from parahydrogen end up in positions which are chemically (but not magnetically) equivalent.

In order to demonstrate this attractive feature, we have investigated the selective hydrogenation of dienes to monoenes with subsequent formation of the alkanes using the cationic complex $[Rh(NBD)(PPh_3)_2]^+PF_6^-$ (NBD = 2,5-norbornadiene) and para-enriched dihydrogen (p-H_2).

When the cationic complex comes into contact with p-H_2 in acetone-d_6 as solvent, the NBD ligand of the catalyst becomes hydrogenated. Fig.1(a) shows the NMR spectrum obtained during the hydrogenation of 6.1mg of $[Rh(NBD)(PPh_3)_2]^+PF_6^-$ with p-H_2 at room temperature in an open system. Fig.1(b) reveals that a similar polarization pattern is observed after addition of 8.5mg of NBD to the reaction products as contained in the above solution upon further hydrogenation. These polarization NMR signals can be assigned to 2-norbornene. This intermediate becomes subsequently hydrogenated to norbornane, which is depicted in Fig.1(c) obtained during the latter stages of the conversion.

Fig.1(a) proves that the NBD ligand of the complex becomes hydrogenated, whereby the 2-norbornene is formed with a concentration too low to be detected by regular NMR. This hydrogenation of a ligand changes the catalytical properties of the complex: it leads to active species, which subsequently hydrogenate NBD to 2-norbornene and 2-norbornene to norbornane. These results are in agreement with those of Schrock and Osborn[10], but here this information can be obtained *in situ* at very low concentration of the complex demonstrating the sensitivity of this method.

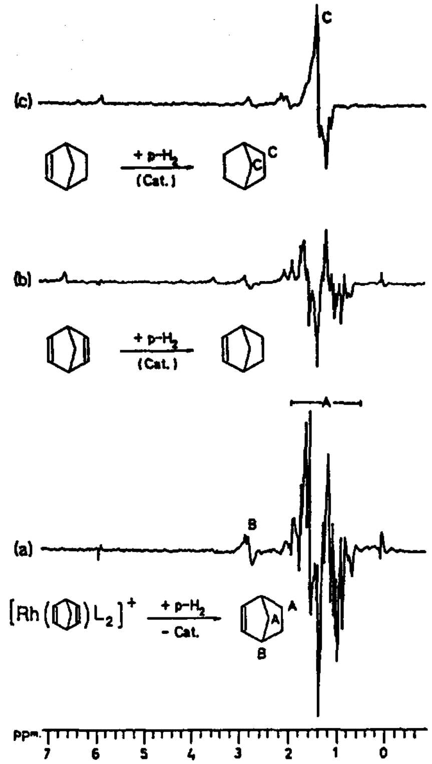

Figure 1: ^{1}H-FT-NMR spectra at 80MHz of the hydrogenations using $[Rh(NBD)L_2]^+PF_6^-$ as catalyst precursor, NBD = 2,5-norbornadiene, L = PPh_3, Cat. = catalytically active species. (a): $[Rh(NBD)L_2]^+PF_6^-$ (6.1mg) dissolved in 1ml acetone-d_6 after hydrogenation with para-enriched H_2 (p-H_2) for 15s. (b): After addition of NBD (8.5mg) and hydrogenation with p-H_2 for 15s; this polarization pattern is observed for about 12min. (c): 150s after the 2-norbornene signals disappear, norbornane signals appear showing polarization as well.

During the hydrogenation of NBD [Fig.1(b)] increasing amounts of 2-norbornene are being formed. Therefore, two substrates enter into competition. In such a case this method can immediately differentiate between the rates of hydrogenation of two different substrates.

In a second example a universal reaction product, namely tetrahydrofuran, is being obtained from two different precursors, i.e. from 2,5-dihydrofuran [Fig.2(a)] or 2,3-dihydrofuran [Fig.2(b)], respectively, using p-H_2 and $RhCl(PPh_3)_3$ (Wilkinson's catalyst) in both cases.

It is interesting to note that even in the case where the 2,5-isomer is converted to THF, polarization signals occur, although the transferred hydrogen atoms derived from parahydrogen occupy chemically equivalent positions in the product. This signifies that a magnetic inequivalence of the transferred hydrogen atoms in the product is sufficient to break the symmetry of parahydrogen, and thus causes nuclear spin polarization. Similar phenomenons have been observed by C. R. Bowers.[11] In addition, both the α- and the β-protons display polarization, wheras one would have naively expected to observe polarization for the β-protons only, i.e. for those protons which stem from the parahydrogen. Instead in either case both the α- and the β-protons display polarization [Fig.2(a) and (b)]. These complications are the consequence of coupled spin systems, which spread the polarization even to those nuclei, which themselves may not stem from the parahydrogen. Furthermore, time dependent effects such as the Nuclear Overhauser Effect (NOE) have to be considered also.

However, a comparision of the NMR polarization spectra depicted in Fig.2 proves that the individual polarization patterns depend characteristically on the position of the transferred hydrogen atoms. Accordingly they reflect the history of the formation of the final product.

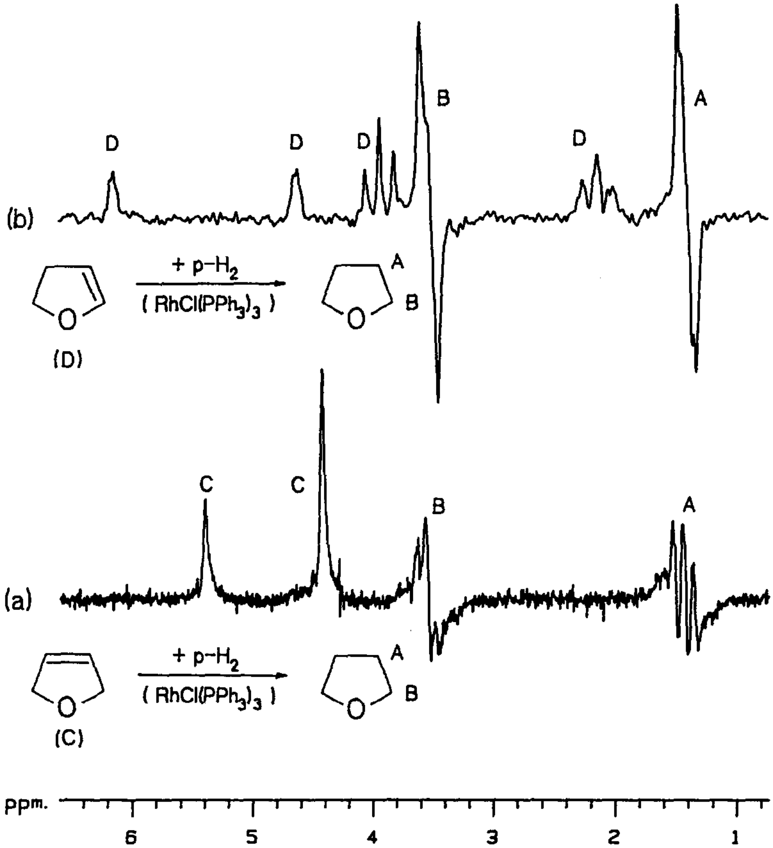

Figure 2: ^{1}H-FT-NMR spectra at 80MHz during the hydrogenations of two different educts to tetrahydrofuran. (a): 2,5-dihydrofuran (50mg) and $RhCl(PPh_3)_3$ (10.5mg) dissolved in 1ml C_6D_6; 50 accumulated spectra; prior to each transient, para-enriched H_2 (p-H_2) was transferrred into the sample for 26s. (b): 2,3-dihydrofuran (25mg) and $RhCl(PPh_3)_3$ (8.8mg) dissolved in 1ml C_6D_6; 20 accumulated spectra; prior to each transient, p-H_2 was transferred into the sample for 55s.

This example demonstrates that it is possible to identify intermediates, which preceeded the reaction product, e.g. intermediates generated by metal catalyzed isomerization of double bonds during the hydrogenation. Since the nuclear spin polarization does not remain confined to those hydrogens derived from the former parahydrogen, a more complex analysis of the polarization spectra of the intermediates is imperative. Nevertheless, this method can reliably identify intermediates or precursors of reaction products in situ like isomeric monoenes during diene hydrogenations as demonstrated here.

These possibilities are currently being further investigated and will be reported in more detail in a subsequent publication.

Experimental Section: These experiments were carried using a 80MHz-FT-^{1}H-NMR spectrometer. Para-enriched hydrogen containing about 50% para-H_2 was prepared by passing H_2 through activated charcoal at 77K and bubbled through a capillary into the spinning NMR-tube containing the reaction solution. All solvents and reagents were used as obtained without further purification.

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