Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Monitoring fast chemical processes by reaction-interrupted excitation transfer (ExTra) NMR spectroscopy

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Complexation

Noteworthy, the magnetization of a certain resonance does not have to be negative in order to be traced. As long as the magnetization did not relax back to equilibrium, a comparison of the integrals of the ExTra NMR spectrum and a normal 1D proton spectrum afterwards reveals the fate of the investigated atom; shown for the complexation of magnesium ions by ethylendiamintetraacetate (EDTA) in Figure S1. The reaction delay d_r (see Figure S1) was set to 1 second.

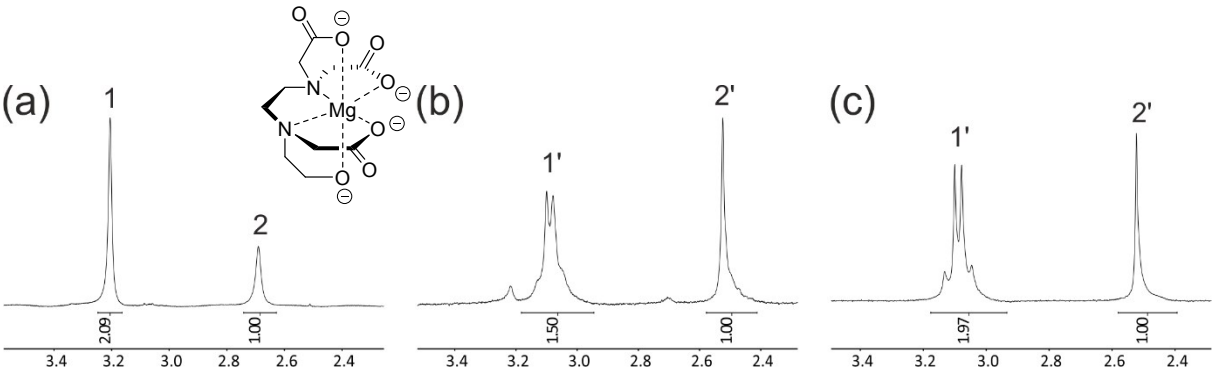

Figure S1. Complexation of magnesium ions by ethylendiamintetraacetat (EDTA): (a) Conventional 1D spectrum of EDTA. The H1-proton at 3.21 ppm is selectively inverted by an 180° Gauss pulse during the ExTra NMR approach. Comparison of the signal intensities of the ExTra NMR sspectrum (b) and a conventional 1D proton spectrum after the reaction (c) allows the easy identification of the previously inverted H1'-proton in the product spectrum. Parameters of spectra (a), (b) and (c): 1 scan, 16k data points, 0.3 Hz exponential window function.

Saturation as an alternative to signal inversion

Instead of peak inversion, saturation of the starting signal would be an alternative. Saturation could even be continued during the ongoing reaction. We compared (a) the inversion approach with (b) presaturation and (c) continuous saturation throughout the reaction. For the pulse program, we replaced the selective 180-degree pulse with a period of decoupling of the selected resonance. While in the inversion experiment both the selected signal and the product peak are negative, in the case of presaturation we can detect small positive educt and product peaks, both produced due to partial relaxation during the reaction delay. For continuous saturation, the educt peak is small and negative while the product peak, again caused by partial saturation, is small and positive. In comparison, the product peaks for all three approaches had very similar integrals. However, the data produced by the inversion experiment more convenient, as an inverted signal is more easily spotted (see Figure S2).

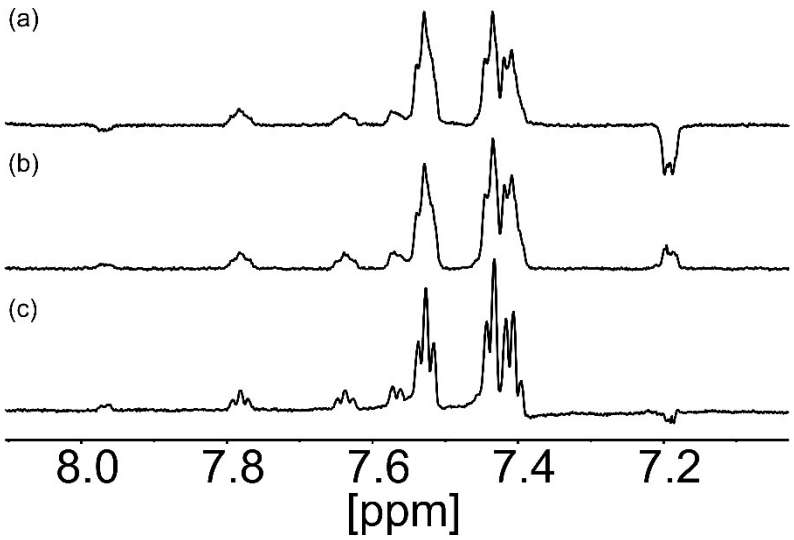

Figure S2. Comparison of the inversion and saturation approaches on the example of diazocine. Reaction time was 1 second. (a) Inversion of the desired signal yields an inverted reactant and product signal. (b) Presaturation in analogy to a steady state type NOESY experiments gives smaller signals in the product. (c) Saturation throughout the whole reaction yields a spectrum where the desired proton displays a negative peak in the reactant and a smaller peak in the product. Parameters of spectra (a) and (b): 1 scan, 16k data points, 0.3 Hz exponential window function.

Pulse program for ExTra monitoring of chemical reactions

```
;ExTra reaction monitoring
;avance-version (07/04/03)
;Excitation Transfer for tracking of single protons during fast reactions
;
;$CLASS=HighRes
;$DIM=1D
;$TYPE=
;$SUBTYPE=
;$COMMENT=


#include <Avance.incl>
#include <De.incl>
#include <Grad.incl>
#include <Delay.incl>

"acqt0=-p1*2/3.1416"
"spoff12=bf1*(cnst19/1000000)-o1"

1 ze
2 30m
  d1 pl0:f1
  (p12:sp12 ph1):f1
  p16:gp5                     ;this gradient pulse indicates the point of injection
  d7 pl1:f1
  p1 ph2
  go=2 ph31
  30m mc #0 to 2 F0(zd)
exit


ph1=0 2
ph2=0 0 2 2 1 1 3 3
ph31=0 0 2 2 1 1 3 3


;pl1 : f1 channel - power level for pulse (default)
;p1 : f1 channel -  90 degree high power pulse
;p2 : f1 channel - 180 degree high power pulse
;d1 :relaxation delay; 1-5 * T1
;d7 : delay for inversion recovery
;NS :8 * n, total number of scans: NS * TD0
;DS :4



;$Id: t1ir1d,v 1.11 2009/07/02 16:40:46 ber Exp $
```

Pulse program for ExTra monitoring of photochemical reactions

```
;ExTra reaction monitoring
;avance-version (07/04/03)
;Excitation Transfer for tracking of single protons during fast photochemical reactions
;
;$CLASS=HighRes
;$DIM=1D
;$TYPE=
;$SUBTYPE=
;$COMMENT=


#include <Avance.incl>
#include <De.incl>
#include <Grad.incl>
#include <Delay.incl>

"acqt0=-p1*2/3.1416"
"spoff12=bf1*(cnst19/1000000)-o1"

1 ze
2 30m
  d1 pl0:f1
  (p12:sp12 ph1):f1
  setnmr3|28
  d7 pl1:f1
  setnmr3^28
  p1 ph2
  go=2 ph31
  30m mc #0 to 2 F0(zd)
exit


ph1=0 2
ph2=0 0 2 2 1 1 3 3
ph31=0 0 2 2 1 1 3 3


;pl1 : f1 channel - power level for pulse (default)
;p1 : f1 channel -  90 degree high power pulse
;p2 : f1 channel - 180 degree high power pulse
;d1 :relaxation delay; 1-5 * T1
;d7 : delay for inversion recovery
;NS :8 * n, total number of scans: NS * TD0
;DS :4



;$Id: t1ir1d,v 1.11 2009/07/02 16:40:46 ber Exp $
```