Eduard Stadler, Anna Eibel, Dmytro Neshchadin and Georg Gescheidt*

Toward Matching Optically and NMR Active Volumes for Optimizing the Observation of Photo-Induced Reactions by NMR

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Abstract: In the recent years photo-induced reactions are becoming increasingly popular in many fields of chemistry comprising biological conversions, material/ environmental science and synthesis. NMR monitoring of such reactions has been shown being advantageous and several strategies of providing an efficient irradiation of the NMR sample have been developed and reported. Here we show that adjusting the optical properties of the investigated solution to the active volume detected by the NMR experiment is valuable. This is shown with the help of three examples comprising photo-isomerization, photo-induced polymerization and CIDNP-detected bond cleavage. Adjusting the photo-active volume to the NMR detectable portion of the sample provides a substantially more realistic kinetic information, background suppression and reduction of thermal and diffusional effects.

Keywords: CIDNP; NMR; photochemistry; photo-induced reactions.

Dedicated to: Kev Salikhov on the occasion of his 80th birthday.

1 Introduction

Photo-induced chemical reactions have undergone a substantial renaissance within the very recent time. Photo-catalyzed and photo-triggered reactions have been established as very valuable protocols for synthesis [1], redox catalysis [2] and materials [3]. There are several approaches for following the course of the corresponding conversions and establishing products *in situ*. However, for monitoring these reactions with the advantage of obtaining a molecular

^{*}Corresponding author: Georg Gescheidt, Institute of Physical and Theoretical Chemistry, TU Graz, NAWI Graz, Stremayrgasse 9, A-8010 Graz, Austria, E-mail: g.gescheidt-demner@tugraz.at Eduard Stadler, Anna Eibel and Dmytro Neshchadin: Institute of Physical and Theoretical Chemistry, TU Graz, NAWI Graz, Stremayrgasse 9, A-8010 Graz, Austria

fingerprint together with kinetic information, NMR spectroscopy is the most valuable method. Accordingly, several experimental setups have been developed to achieve an efficient monitoring of photo-induced processes inside NMR spectrometers. Sample illumination is, in most cases, accomplished by coupling the light source to optical fibers, which are inserted into the NMR sample tube [4, 5]. A rather extended overview was presented by Kuprov and Hore [6], who developed a stepwise tapered optical fiber for a uniform illumination of samples. The photo-isomerizations of azobenzene derivatives have been investigated using optical fibers [7] and recently different irradiation procedures were evaluated in terms of following environmental processes [8]. It is crucial introducing a sufficient light intensity into the NMR sample. However, one also has to bear in mind that the active volume of the photo-induced reaction does not match the portion of the sample detected by NMR. Indeed, in many cases, the light gets absorbed in a region very close to the area of irradiation and, accordingly, the NMR spectrum becomes substantially contaminated by a background stemming from signals of the unreacted/non-irradiated portion of the sample (Figure 1).

A somehow reversed aspect was followed obtaining optical spectra *in situ* inside NMR spectrometers. When the NMR sample possesses a rather high optical density the optical path of the light has to be made smaller. In such cases, polytetrafluoroethylene inserts were placed inside NMR tube (lower part) to produce thin, optically-transparent layers for achieving a short path length and obtaining reasonable optical spectra; the insert additionally served as a mirror for a reflection probe [9].

In our projects, we have been performing experiments which require an efficient irradiation of the sample inside the NMR spectrometer [10–14]. In particular, photo-CIDNP experiments necessitate sufficient pre-saturation, to reduce background signals. However, artifacts stemming from resonances from



Fig. 1: NMR tube and irradiated region (cross section). Left: irradiation source from the side outside the NMR tube, as used in this work, right: irradiation source inside the NMR tube e.g. by optical fibers.

non-irradiated regions of the NMR tube may occur. We have, therefore, tested a rather simple setup, which can be combined with various irradiation sources (see Figure 1 and reference [6]). It consists of a standard NMR tube with a narrower tube inserted into it (double-tube setup, DTS, Figure 2). The solution that is investigated occupies the space between the two tubes. The advantage of this setup is that the diameter of the inserted tube can be adjusted to the optical density of the reaction solution thus providing that the irradiated volume matches that detected by NMR. In the present study a quartz rod serves as a light guide, and the sample is irradiated from the side. We will show the advantages of this setup on three examples. The usability is not just limited to CIDNP but also to photo-induced processes followed by NMR. Accordingly, the first example is the well-described photo-isomerization of azobenzene from its E isomer towards its Z isomer [7], the second indicates the product formation within a photo-induced radical polymerization and finally we describe CIDNP spectra taken upon photocleavage of 2-hydroxy-2-methyl-1-phenylpropan-1-one, a commercially-available photoinitiator (Darocur 1173) for radical polymerization.

2 Results and discussion

2.1 E/Z-Azobenzene

The ¹H-NMR spectrum of *E*-azobenzene (Scheme 1) presents a multiplet around 7.9 ppm (*ortho* protons), a multiplet at 7.55 ppm (*para, meta* protons). For the *Z* isomer a multiplet around 7.2 ppm (*para* and *meta* protons) and a multiplet at 6.8 ppm emerge.



Fig. 2: (a) DTS setup (b) Inner tube, lifted sample volume around 150 μ L.

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Scheme 1: *E*- and *Z*-isomers of azobenzene.



Fig. 3: ¹H-NMR monitoring of the photo isomerization of *E*/*Z*-azobenzene. Left: Spectra taken after (a) 30 s, (b) 60 s and (c) 7 min in DTS samples; right: corresponding spectra taken in conventional NMR tubes.

In Figure 3 we compare the NMR spectra obtained upon irradiation for 30 s, 60 s, and 7 min. Clearly, the "double-tube setup" (DTS) reveals well distinguishable conversion after 30 s whereas, the "usual" setup (i.e. conventional NMR tube instead of the DTS) indicates a 3-times lower conversion (Figure 3, right trace). These differences can be straightforwardly traced back to the substantially more pronounced background signal of non-reacted *trans*-azobenzene, i.e. the

dominating segment of the sample, which is not irradiated. At longer irradiation periods, the differences between the DTS and the "usual" setup become less pronounced. This can be traced back to diffusional processes and heat transfer.

2.2 Photo-initiated radical polymerization

Photo-initiated radical polymerization has been an exceedingly successful technique for obtaining rapidly curing surfaces and for 3D structures [15–21]. Such reactions can be monitored by thermal analysis (e.g. photo DSC) and infra-





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red spectroscopy, however only NMR is the method of choice when rather precise information at a molecular resolution is required. Such investigations have to be performed at early stages of the polymerization since the products should be soluble to provide a straightforward NMR fingerprint, which is not deteriorated by intense line broadening. It is also important to avoid too exaggerating irradiation since follow-up reactions of the polymerized material may occur. We have, therefore chosen following a standard photopolymerization at a secondsto-minutes time scale. To this end we have photolyzed a mixture of butyl acrylate (see Figure 4, bottom) and the bisacylphosphine oxide (phenylphosphoryl) bis(mesitylmethanone) (BAPO) in acetonitrile. With the extinction coefficient of the BAPO being 795 L*mol⁻¹*cm⁻¹ (55 mM) ca. 90% of the light is absorbed by the thin (1 mm) liquid layer. The conversion was monitored using both sampletube setups. Figure 4 presents the conversion of the educts (bottom, see the colorcoded assignment of the signals) to the polymer. Here the proton resonance at 3.9 ppm assigned to the two protons adjacent to the oxygen of the ester group attached to the growing polymer chain and the decaying signals of the alkene protons between ca. 6.3 and 5.6 ppm are the most prominent and clearly distinguishable signals. The integrals of these latter resonances vs. time are presented in Figure 5. Whereas only an initial conversion can be detected after 5 min in the usual setup, the DTS indicates basically full conversion. The plateau observed in the usual setup is probably caused by an initial drop of the signal intensity due to relaxation effects of photo-initiator radicals. This translates into a half-life (t_{ij}) of butyl acrylate being ca. 8 s for the DTS whereas irradiation in the conventional



Fig. 5: Time profile for the depletion of the NMR signals attributed to $H_{a,b,c}$ of butyl acrylate using a conventional NMR tube (blue) and the DTS (red). The insert shows the decay for the DTS sample at an extended scale.

Brought to you by | Cornell University Library Authenticated Download Date | 10/18/16 11:10 AM NMR tube suggests $t_{1/2}$ = 414 s; a factor of 51! (Figure 5) Accordingly the DTS reflects the kinetics for the formation of the photopolymer to a much more realistic extent. As for the first example, the particular advantage of DTS is that the photoreaction is confined to a volume basically compatible with the NMR-active area.

2.3 Photo CIDNP

Photo CIDNP spectroscopy has been a valuable tool for observing rather rapid photo-triggered chemical reactions [22]. Many investigations have been dedicated to early events in photopolymerizations particularly, the mechanism and the follow-up reactions of the initiating radicals (Scheme 2) [23–25]. We have tested the DTS for the well-established cleavage of 2-hydroxy-2-methyl-1-phenylpropan-1-one.

CIDNP spectroscopy requires an efficient saturation of the NMR spectrum before irradiation with light produces a radical (ion) pair leading to polarized NMR resonances (Scheme 3).

As a result, the observed CIDNP intensities may be influenced (beside the wellknown spin dynamics) [22, 26–28] by incomplete saturation and by a substantial portion of unreacted substrate(s). In Figure 6, we compare the DTS with CIDNP performed with the use of a conventional NMR tube. The extinction coefficient of Darocur 1173 in acetonitrile- d_3 is 22 L*mol^{-1*}cm⁻¹. This results in absorbance of 90% light intensity in a layer of 1.4 mm at the used concentration of 330 mM. In our DTS setup, the cross section of the liquid layer was 0.15 mm; accordingly the light beam passed through the entire solution.



Scheme 2: Cleavage of 2-hydroxy-2-methyl-1-phenylpropan-1-one.



Scheme 3: CIDNP sequence (for τ_1 and τ_2 , see Experimental part).



Fig. 6: NMR spectrum and CIDNP spectra of 2-hydroxy-2-methyl-1-phenylpropan-1-one upon photolysis at 355 nm (for details, see Experimental part). The CIDNP and dummy spectra are depicted on the same scale (compensated for different receiver gains). Squares indicate substantial differences in the spectra using conventional tubes and the DTS.

The particular advantage of the DTS can be easily distinguished by comparing the "dummy" experiments with the irradiation source blocked representing the quality of the background signal (in terms of pre-saturation). Figure 6 shows that in particular, the signals of the aliphatic protons can hardly be saturated in the conventional NMR tube at concentrations around 100 mM. However, application of the DTS markedly decreases the background (Figure 6, bottom) producing better distinguishable lines in the CIDNP spectrum (Figure 6, bottom left). Our example represents an ideal case for the CIDNP technique presenting strong polarizations, but when the polarization pattern gets more complex and polarization patterns become weaker the quality of the background signal becomes more critical.

3 Summary and conclusions

Our investigations reveal that the "tube in the tube" (DTS) technique presents a simple but valuable approach of getting NMR information of photo-induced reactions and their products. When the DTS is used, the active photochemical volume can be adjusted to the NMR-detection volume. This procedure clearly does not increase the signal-to-noise ratio of the NMR signal but leads to a substantial decrease of background effects. Our kinetic investigation following the photo-induced radical polymerization of butyl acrylate well illustrates this effect. This advantage is accompanied by the fact that a substantially shorter time of irradiation is necessary for clearly distinguishing NMR resonances of photoproducts since they are less masked by those of the educts. Moreover since less energy has to be transferred to the sample, thermal effects are basically undetectable. The chemical advantage of this approach is that it becomes less likely the primary products undergo undesired follow-up reactions.

We have tested our setup using a wide-bore probe head and irradiation from one side (Figure 1), which is of advantage, since the sample can be rotated during the experiment. However, the DTS can easily be applied also in spectrometers with a standard probe head with inserted fibers of any shape. The DTS could also be used for implementing UV-VIS detection in NMR spectroscopy; if the inner tube is coated or replaced by a material that reflects light into an optical fiber that is connected to a detector as developed by Tolstoy et al. [9]. This approach would also ensure the matching of the UV-VIS and NMR detected volumes. Generally this setup allows adjusting the size of the inner tube to the optical density of the investigated solution providing a close to ideal optical path for the irradiation experiment.

4 Experimental

4.1 Materials

Azobenzene was obtained from Sigma Aldrich (purity 98%) and was used without further purification. Twenty millimolar samples of azobenzene in acetonitrile- d_3 (Euriso-top, used as received) were prepared. Darocur® 1173 was purchased from MERCK and used as delivered. BAPO (commericialized as Irgacure 819, Ciba) and butyl acrylate (Fluka, filtered with aluminum oxide powder shortly before use) were used as obtained. NMR measurements were performed either in conventional NMR tubes or in the double tube setup. In the double tube setup, an EPR tube filled with the solvent (acetonitrile- d_3) is placed inside the NMR tube, which contains the sample.

4.2 Azobenzene

¹H NMR spectra were recorded on a 200 MHz Bruker AVANCE DPX spectrometer. A Hg–Xe UV lamp (Hamamatsu Lightningcure LC4, 3500 mW/cm², λ_{max} = 365 nm) was guided into the NMR spectrometer using a quartz rod. 1D ¹H NMR experiments (32 scans) were performed after different irradiation times (between 30 s and 7 min). Chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) using the residual deuterated solvent signals as an internal reference (acetonitrile- d_3 , δH = 1.94 ppm).

4.3 Polymerization experiments

Butylacrylate was pushed through a syringe filled with AlO powder to remove any stabilizers prior to the photoexposure. A solution of 3+7 (v+v) of butylacraylate and acetonitrile- d_3 containing BAPO (55 mM) was prepared. All samples were measured under atmospheric conditions, i.e. were not degassed.

The inner tube was filled with acetone- d_6 for better shimming and for the spectrometer lock. The NMR tube was irradiated during the NMR experiments continuously with a low power LED (2 mW) with an emitting wavelength of 365 nm operated at a current of 30 mA. The LED was put in direct contact with the quartz rod. (Acquisition and processing parameters: NMR tube: One spectrum was recorded every 20 s. Parameters: aq = 2 s, p1=0.33*4.2, rg = 32, data points = 4 k, filled to 8 k. DTS: One spectrum was recorded every 2.5 s. Parameters: aq = 2 s, p1=0.33*4.2, rg = 400, data points = 4 k, filled to 8 k.)

For obtaining the kinetic traces the pseudo 2D spectra were displayed in absolute value mode and integrated from 5.5 to 6.5 ppm (protons of acryl moiety, 3 H).

4.4 CIDNP of 2-hydroxy-2-methyl-1-phenylpropan-1-one

The concentration was 1+19 (v+v, photoinitiator + acetonitrile- d_3 , ≈ 0.33 M). For the conventional setup the sample volume is 700 µL, for the inner tubing system (DTS) the needed volume is 150 µL. The extinction coefficient of Darocur 1173 at the wave lenght of the used laser (355 nm) was determined to be 22 L*mol^{-1*}cm⁻¹. (Acquisition and processing parameters: presaturation period = 15 s, presaturation pulse power 42 dB, pulse length = 440 µs, ns = 1, rg = 20 (normal NMR tube) and rg = 400 (DTS), p1 = 4.1 µs, at = 3.42 s, data points: 8 k, zero filled to 16 k, added linebroadening LB = 1 Hz. All spectra were baseline corrected. Delay between

presaturation period and laser flash $T_1 = 252 \,\mu$ s, delay between laser flash and rf-pulse $T_2 = 70 \,\mu$ s).

4.5 UV-VIS spectroscopy

UV-Vis spectroscopy was performed using a Shimadzu UV-3101PC UV-Vis-NIR scanning spectrophotometer. The concentration of azobenzene was 1 mM in acetonitrile. The measurement was performed at ambient temperature.

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