

## Facile Quantum Yield Determination via NMR Actinometry

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**Supporting Information** 

**ABSTRACT:** A simplified approach to quantum yield ( $\phi$ ) measurement using in situ LED NMR spectroscopy has been developed. The utility and performance of NMR actinometry has been demonstrated for the well-known chemical actinometers potassium ferrioxalate and o-nitrobenzaldehyde. A novel NMR-friendly actinometer, 2,4dinitrobenzaldehyde, has been introduced for both 365 and 440 nm wavelengths. The method has been utilized successfully to measure the quantum yield of several recently published photochemical reactions.



n recent years, photochemistry has experienced a so-called "golden age", rapidly advancing the field of organic synthesis. The exploration of photochemical reactivity has opened up uncharted chemical space with the invention of cutting-edge chemical transformations facilitating access to novel chemical entities.<sup>1</sup> Despite great advances in the field, detailed mechanistic investigations have been sparse. LED-based NMR illumination devices have been introduced as a simple and powerful tool to obtain valuable and rich kinetic and structural insights into photochemical reactions.<sup>2</sup>

One of the most fundamental parameters in photochemistry is quantum yield ( $\phi$ ). Quantum yield is a measure of efficiency with which absorption of a photon results in a desired chemical transformation. These data can be used to identify whether a radical-chain mechanism may be operable, in which case absorption of a single photon may result in the production of more than one molecule of product.<sup>3</sup> One widely utilized actinometry model system is based on photodecomposition of ferrioxalate ion.<sup>4</sup> However, the protocol is very tedious, requires complete darkness or the use of deep red light at all stages, and is associated with inherent sample manipulation errors and analyst variabilities.<sup>5</sup> Direct NMR detection would offer a much simpler protocol with minimal sample manipulation since all data points for an analysis are taken directly on a single sample. Herein, we describe a comprehensive methodology for quantum yield determination via in situ LED NMR analysis. The developed method is demonstrated on several chemical actinometers, including well-known ferrioxalate and o-nitrobenzaldehyde (o-NBA),<sup>6</sup> as well as 2,4-dinitrobenzaldehyde (2,4-DNBA), a novel actinometer developed in the course of this work.

Derived from the Beer-Lambert law, the rate of disappearance of an actinometric compound (Act) under incident light is governed by eq 1.6

$$-\frac{\mathrm{d}[\mathrm{Act}]}{\mathrm{d}t} = I_0 \phi(1 - 10^{-\varepsilon b[\mathrm{Act}]})$$
(1)

With sufficiently high molecular absorptivity  $\varepsilon$  (M<sup>-1</sup> cm<sup>-1</sup>) and light path length b (cm), eq 1 simplifies to eq 2.

$$I_0 = \frac{k_0}{\Phi} \tag{2}$$

In this case, the expression becomes independent of the concentration of the actinometric compound, and the light intensity is simply measured as the fraction of the zeroth order kinetic constant  $k_0$  (mol L<sup>-1</sup> s<sup>-1</sup>) and the quantum yield. While the assumption above is true for a typical photochemistry setup, that is not the case for NMR actinometry: the light path length in the LED-illuminated NMR device is 1.1 mm, which could be 10-20 times shorter than a conventional photochemical cell. Furthermore, high concentrations of the actinometer can result in an increase in the solution viscosity, potentially resulting in line broadening of signals in the NMR spectrum. For this reason, concentration should be considered when designing NMR actinometry experiments.

The use of o-NBA as a chemical actinometer is well-known, and a quantum yield of 0.5 has been reported over its absorption spectral region of 300-410 nm (Scheme 1).<sup>6</sup> For

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Scheme 1. Photochemical Transformation of *o*-Nitrobenzaldehyde to *o*-Nitrosobenzoic Acid in Ultraviolet Light



our use, we chose an UV LED source with a peak emission at 365 nm. Our strategy required the measurement of initial rates<sup>7</sup> for the reaction of *o*-NBA at increasing concentrations, until the maximum rate is reached and increasing concentrations no longer change reaction rates (Figure 1). These data were then



Figure 1. Experimental (blue circles) and fitted (red line) plot of initial rates (mM/min) versus different  $[o-NBA]_0$  (mM) for the reaction of Scheme 1.

fitted explicitly into eq 1, allowing extraction of both unknowns, namely, the molecular absorptivity ( $\epsilon$ , 265 M<sup>-1</sup> cm<sup>-1</sup>) and the light intensity ( $I_0$ , 23.4  $\mu$ einstein L<sup>-1</sup> s<sup>-1</sup>) (see Supporting Information for details). Our fitted molecular absorptivity matched the published value for *o*-NBA (260 M<sup>-1</sup> cm<sup>-1</sup>), thus providing an independent validation for the method.

With the light intensity ( $I_0$ ) of the 365 nm LED source measured, we began investigating the applicability of NMR actinometry for quantum yield determination. For this purpose, we chose the direct photocatalytic C–H fluorination of leucine methyl ester<sup>8</sup> (Scheme 2). To apply eq 2, the zeroth order

# Scheme 2. Direct Photocatalytic C–H Fluorination of Leucine Methyl Ester



kinetic constant ( $k_0$ ) must be determined. Photoredox catalysts often possess high molar absorptivities (for example,  $\epsilon_{325} = 1.35 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  for  $[W_{10}O_{32}]^{4-}$ ).<sup>9</sup> Therefore, we are usually operating close to the maximum achievable rate limit and a change of the concentration of these photocatalysts would be sufficient to confirm whether we are in the rate plateau region. In this case, the same initial rate was obtained using either 2.5 or 10 mol % of the catalyst and a quantum yield of 0.22 was calculated (see the Supporting Information for details).<sup>10</sup>

The convenience and practicality of NMR actinometry were highlighted when we noticed that light intensity of the 365 nm LED deteriorated somewhat after prolonged usage. Having characterized the concentration dependence, a single measurement with 90 mM or higher concentration of *o*-NBA is sufficient since its reaction rate plateaus at these concentrations (Figure 1). Simple recalibration of the light intensity before and after the actual reaction can be performed (see the Supporting Information for details). The same simplified calibration strategy can be applied for any new LED source.

Unfortunately, while convenient for NMR measurements, *o*-NBA is limited to a 300–410 nm spectral range. We sought to extend the scope of NMR actinometry to include a 440 nm wavelength, widely used for visible-light photoredox catalysis.<sup>11</sup> *o*-NBA does not have any appreciable absorption at this wavelength, but the addition of an electron-withdrawing group could produce the desired red-shift in absorption.<sup>12</sup> For such purpose, we investigated 2,4-dinitrobenzaldehyde (2,4-DNBA) as a commercially available chemical actinometer suitable for 440 nm photochemical reactions (Scheme 3).

#### Scheme 3. Photochemistry of 2,4-Dinitrobenzaldehyde



LED–NMR studies showed that 2,4-DNBA undergoes the same chemical transformation when subjected to 365 or 440 nm light. Despite the presence of two nitro groups, a single 2-nitroso product was formed at both wavelengths. The structure of the 2-nitroso product has been confirmed using 2D NMR data (see the Supporting Information for details). The concentration dependence of initial reaction rates for 2,4-DNBA was measured for both wavelengths (Figures 2 and 3). As expected, the molecular absorptivity at 365 nm was significantly higher than that at 440 nm: 611.5 and 23.4  $M^{-1}$  cm<sup>-1</sup>, respectively.



**Figure 2.** Experimental (blue circles) and fitted (red line) plot of initial rates (mM/min) versus different [2,4-DNBA]<sub>0</sub> (mM) for the reaction of Scheme 3 at 365 nm.

The light intensity of the 365 nm LED source calibrated with *o*-NBA was used to calculate the quantum yield for 2,4-DNBA (eq 2), which turned out to be 1.00 (see the Supporting Information for details). Determination of the quantum yield for 2,4-DNBA at 440 nm required measuring the light intensity of the 440 nm LED source. Ferrioxalate, a well-characterized and broadly utilized actinometer with a range of wavelengths 250–500 nm,<sup>13</sup> was utilized for this purpose. Using classical ferrioxalate actinometry protocol,<sup>14</sup> the light intensity of the 440 nm LED source was determined to be 75.3  $\mu$ einstein L<sup>-1</sup>s<sup>-1</sup> (see the Supporting Information for details). The



Figure 3. Experimental (blue circles) and fitted (red line) plot of initial rates (mM/min) versus different [2,4-DNBA]<sub>0</sub> (mM) for the reaction of Scheme 3 at 440 nm.

quantum yield for 2,4-DNBA at 440 nm was thereby calculated to be 0.08.

With its quantum yield and molecular absorptivity determined, 2,4-DNBA can be used as an NMR-friendly chemical actinometer for both 365 and 440 nm wavelengths. To demonstrate its utility, we repeated the recently published photocatalytic dehydrogenation of indoline<sup>14</sup> (Scheme 4) using

#### Scheme 4. Photoredox Indoline Oxidation



440 nm LED–NMR. The quantum yield of this reaction calculated with 2,4-DNBA as an NMR actinometer (see the Supporting Information for details) was in a good agreement with the previously reported value obtained using the classical ferrioxalate method: 0.38 and 0.40, respectively.<sup>15</sup>

The tedious nature and impracticality of the traditional ferrioxalate protocol prompted the development of the NMR-friendly 2,4-DNBA actinometer described in this work. However, ferrioxalate is still the most broadly utilized actinometer with a superior range of wavelengths (250–500 nm). Classical ferrioxalate actinometry (Scheme 5) requires

## Scheme 5. Photodecomposition of Ferrioxalate Ion Solution

$$2[Fe(C_2O_4)_3]^{3-} \xrightarrow{250 - 500 \text{ hm}} 2 Fe(C_2O_4) + 3[C_2O_4]^{2-} + 2CO_2$$

further derivatization of the weakly absorbing photolysis products to strongly absorbing compounds,<sup>4</sup> which is both cumbersome and leads to inherent measurement errors.<sup>5</sup> Thus, we envisioned that direct NMR detection would considerably streamline the experimental setup and lower experimental errors.

As is evident from Scheme 5, this system does not contain any <sup>1</sup>H nuclei suitable for NMR detection. Furthermore, the presence of iron ions introduces a significant degree of paramagnetism, which leads to line-broadening due to faster relaxation rates. Initial NMR studies showed that  $CO_2$  gas generated in the reaction is dissolved in the reaction mixture in detectable concentrations, suggesting the use of <sup>13</sup>C NMR for the actinometry. For <sup>13</sup>C NMR detection, we were able to use paramagnetism to our advantage, capitalizing on very short relaxation delays typical for paramagnetic NMR to detect high quality <sup>13</sup>C NMR spectra in a matter of minutes. As a proof of concept, a <sup>13</sup>C NMR spectrum was acquired in 8.5 min with 8192 transients for a  $CO_2$  enriched sample prepared by dissolving dry ice in the standard ferrioxalate solution (Figure 4). The presence of dissolved  $CO_2$  is evidenced by a characteristic <sup>13</sup>C chemical shift of ~124 ppm.



200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

**Figure 4.** <sup>13</sup>C NMR spectrum of a solution of  $K_3[Fe(C_2O_4)_3]$  (0.15 M) in 0.05 M H<sub>2</sub>SO<sub>4</sub> in D<sub>2</sub>O, with added 1% v/v MeCN (as a reference) and CO<sub>2</sub> (from dry ice). D1 = 1 ms; AQ = 49 ms, DS = 512, NS = 8192; total acquisition time is 8.5 min.

Using LED-NMR to irradiate potassium ferrioxalate solution at 440 nm, we confirmed that  $CO_2$  formed during the reaction is detectable as a dissolved gas (Figure 5).  $CO_2$ 



**Figure 5.** <sup>13</sup>C NMR spectra tracking the photodecomposition at 440 nm of a solution of  $K_3[Fe(C_2O_4)_3]$  (0.15 M) in 0.05 M H<sub>2</sub>SO<sub>4</sub> in D<sub>2</sub>O. Each spectrum is acquired with D1 = 1 ms; AQ = 49 ms, DS = 512, NS = 8192 for a total acquisition time of 8.5 min.

accumulates in solution until the concentration limit is reached and bubbles begin to form, leading to deterioration of both lock level and a line shape. Direct measurement of the initial  $CO_2$ formation rate by NMR was conducted by using data points before the solubility limit was reached. Although finding a quantitative <sup>13</sup>C NMR reference for  $CO_2$  under the exact reaction environment was not feasible,<sup>16</sup> one can convert  $CO_2$ integrals in <sup>13</sup>C NMR spectra into concentrations using known reaction rates.

Potassium ferrioxalate photochemistry was conducted using LED–NMR irradiation at 365 and 440 nm. Data acquired at 365 nm were used to reference <sup>13</sup>C NMR integrals of the CO<sub>2</sub> resonance utilizing the known light intensity of the 365 nm LED source (via *o*-NBA) and known ferrioxalate quantum yield at 365 nm<sup>4</sup> (see the Supporting Information for details). This referencing was subsequently used to calculate the  $I_0$  of the 440

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nm LED light source (see the Supporting Information for details). The results were in good agreement with the previous measurement conducted using traditional ferrioxalate protocol: 80 and 75  $\mu$ einstein L<sup>-1</sup> s<sup>-1</sup>, respectively.

To summarize, we have demonstrated the viability of direct LED-NMR measurements for facile and accurate quantum yield determination. We have developed a simple and convenient NMR actinometry protocol, which has been validated with two well-studied chemical actinometers, onitrobenzaldehyde and ferrioxalate. We have introduced an NMR-friendly chemical actinometer, 2,4-dinitrobenzaldehyde, with a superior range compared to the o-nitrobenzaldehyde, that enabled NMR actinomtery at 440 nm. The applicability of this methodology has been demonstrated using two recently reported photochemical transformations. Finally, we have developed a direct LED-NMR approach for ferrioxalate actinometry, which significantly streamlines and simplifies experimental procedures compared to the classical ferrioxalate actinometry protocol. We believe that the NMR actinometry framework developed in this work will become a useful tool in the field of photochemistry.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.8b00391.

Experimental procedures, data analysis, and spectroscopic data of new compounds (PDF)

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## Notes

The authors declare no competing financial interest.

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(15) An LED light source at 440 nm has been found to be relatively stable over time; therefore, the recalibration of the light intensity before and after the reaction is recommended but not required.

(16) Relaxation time of nuclei used for quantification is a very important yet very difficult to control parameter. Very short recycling delays used in paramagnetic <sup>13</sup>C NMR experiments allow high sensitivity but exacerbate the differences in relaxation times if one tries using external concentration reference. Unfortunately, in the presence of a paramagnetic agent NMR relaxation times of different molecules are strongly influenced by a degree of its interaction with such paramagnetic agent. Matching relaxation times of the concentration reference and of the analyte was found to be practically impossible.