Multiple wavelength (365–475 nm) complete actinometric characterization of Corning® Lab Photo Reactor using azobenzene as a highly soluble, cheap and robust chemical actinometer

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Abstract

The characterization of commercially available Corning® Lab Photo Reactor by actinometry at different wavelengths (365, 385, 405 and 475 nm) using azobenzene $E \leftrightarrow Z$ photoisomerization is reported. By comparison with photon fluxes determined externally using a radiometer, this method based on NMR spectroscopy is rapid, cheap, robust, reproducible and can be applied to UVA–visible range, compared to previously described chemical actinometric protocols. Recalculation of isatin N^2 -phenylhydrazone isomerization quantum yield at 405 nm gave almost the same value as the literature data ($\Phi = 0.0013$) and confirmed the robustness and applicability of this methodology.

Keywords Azobenzene actinometry · Continuous photochemistry · Quantum yield determination

1 Introduction

The development of continuous flow photoreactors has recently demonstrated higher efficiencies compared to batch systems [1–5]. Indeed, the photoreactor optical path length miniaturization enhances considerably the local volumetric rate of photon absorption (LVRPA) for a large variety of chemical transformations, and in addition by operating in continuous mode the high level of reproducibility of reaction times gives access to precise kinetic measurements [6]. Today, with the development of monochromatic, long life and low consumption light sources, such as high power LEDs [7], a new generation of particularly efficient commercially available flow photoreactors is appearing on the market, and for which the productivity varies from the lab scale (few g per hour) up to the industrial scale (tons per day). In such context, the development of low cost and versatile actinometric procedures is highly required in order to

quantify the photon flux density passing through the photoreactor, to characterize precisely how evolves the photoreactor itself with time in case of productivity variations and for maintenance operations. Unfortunately, few actinometric protocols for the determination of the received photon flux density within flow microphotoreactors has been reported and most of them are based on costly actinometers with tedious procedures. [8–13]

In a more fundamental context or for scale-up approaches, [14] actinometry is necessary for the determination of photochemical reactions quantum yield, [15–18] which is the physical parameter governing the reactivity. Indeed, the quantum yield represents the ratio between the number of molecules transformed and the number of absorbed photons at a certain wavelength in a period of time. Knowing the value of the quantum yield also helps understand the photo-reaction mechanism [19].

The measurement of incident absolute photon flux density (I_{photon} in $\text{ein.s}^{-1}.\text{m}^{-2}$) passing through a photochemical reactor can be realized using electronic devices (photodiodes, radiometers, spectrometers); nevertheless, for flow photochemical reactors, the optical path is usually miniaturized (from 0.4 to 1.5 mm) and the implementation of such measurement tools inside the photoreactor is rendered particularly difficult. Prolonged contacts with the reaction solution could also alter its performances with time. The problematic is similar in batch reaction media of small

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dimensions, and as a consequence, chemists have studied a large range of substances that undergoes first-order rate law light-induced reactions and for which the rate of the photo-induced transformation into another specie can be measured precisely and correlated with the incident absolute photon flux density according to a physical model. [20] In such systems, the absorbance is varying with the time since the photo-precursor R and the photo-product P are both absorbing with different molar extinction coefficients (ϵ in $\text{mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$). In order to determine precisely quantum yield of these photoreactions, calibrated electronic devices have been employed. [21] Absolute measurement of incident irradiance at a certain wavelength (Q_0 in $\text{W} \cdot \text{m}^{-2}$) is proportional to the absorbed photon flux density over the entire surface of the system on a certain period of time (ΔI_{Abs} in $\text{ein} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$). For chemical systems for which the absorption of photon is high enough (up to 99%), measuring the reaction rate allows the calculation of the absorbed photon flux according to the three following equations:

$$Q_0 = I_0 \times \frac{h \times c \times N_A \times l}{\lambda \times V} = I_{\text{photon}} \times N_A \times E_{\text{photon}}, \quad (1)$$

$$\nu = -\frac{dR}{dt} = \frac{dP}{dt} = dI_{\text{Abs}}/dt \times \Phi, \quad (2)$$

$$dI_{\text{Abs}}/dt = I_{\text{photon}} (1 - 10^{-dA(\lambda)/dt}), \quad (3)$$

which can be written after Taylor series expansion [7] if $\Delta A(\lambda) < 0.2$ as

$$dI_{\text{Abs}}/dt = I_{\text{photon}} \times \ln(10 \times dA(\lambda)/dt). \quad (4)$$

By combining those three equations we obtain the following equation:

$$Q_0 = \frac{\nu \times N_A \times E_{\text{photon}}}{\ln(10 \times dA(\lambda)/dt \times \Phi)}, \quad (5)$$

where ν is the rate of photon absorption by the substance R in s^{-1} , ΔI_{Abs} is the absorbed photon flux density at the reaction wall in $\text{ein} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$, I_0 is the incident photon flux in $\text{ein} \cdot \text{s}^{-1}$, I_{photon} is the absolute photon flux density at the reaction wall in $\text{ein} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$, $\Delta A(\lambda)$ is the absorbance variation of the system at a certain wavelength λ over time, Φ is the quantum yield of the photochemical reaction, $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ is the Avogadro's number, $h = 6.63 \times 10^{-34} \text{ J} \cdot \text{s}^{-1}$ is the Planck constant, $c = 299.92.58 \text{ m} \cdot \text{s}^{-1}$ is the speed of light in vacuum and E_{photon} in J is the energy of one incident photon at a certain wavelength.

When using chemical actinometry for photon flux density determination in Corning® Lab Photo Reactor, the main difficulty concerns the reactor walls equipped with thermal management system composed of 3 layers (soda lime glass,

thermal fluid (usually water), soda lime glass) which limit the light transmission to the reaction medium by refraction and absorption, and consequently, the actinometric measurement will give access to the transmitted absolute photon flux $I_{\text{photon(transmitted)}}$ inside the reaction channel (Fig. 1). The transmitted photon flux can be calculated from the absolute photon flux of the light source using the overall transmission of the reactor wall according to the following equation:

$$I_{\text{photon(transmitted)}} = I_{\text{photon(light source)}} \times T\%. \quad (6)$$

As a consequence, applying previous Eqs. (1–5) gives access to the transmitted irradiance inside the reactor $Q_{0(\text{transmitted})}$. In order to correlate data measured by actinometry ($Q_{0(\text{transmitted})}$ in $\text{W} \cdot \text{m}^{-2}$) with data measured by radiometry ($Q_{0(\text{emitted})}$ in $\text{W} \cdot \text{m}^{-2}$), the calculation should take into account the total transmission of the reactor wall, including every layers ($T\%$) similarly than for Eq. 6.

Another important aspect to mention concerns the geometry of Corning® Lab Photo Reactor channel which presents two parallel walls oriented perpendicularly to the light source; since the optical path is constant at every point of the channel, and the distance to the light source fixed and constant, Eqs. (1–5) can be directly used. When using chemical actinometry for photon flux determination in fluidic reactor, since the optical path is much smaller (in the μm – mm range), the absorption is lowered, and consequently, more concentrated solutions of actinometer could be used in opposition with batch systems for which usually diluted solution has been employed due to larger dimensions and absorption. When performing actinometry, the optimum case concerns systems for which the absorption is nearly constant over time which allows to simplify equations. Nevertheless, when the absorbance varies with time it is necessary to measure precisely the molar extinction coefficients of the photo-precursor and of the photo-product to later quantify the concentration and the absorbance evolution using UV–visible spectroscopy. In the physical model, we clearly found that both the rate of photon absorption and the absorption variation are connected, inducing some complex relationship when both the photo-precursor and the photo-product are reversible under photo-excitation. In any case it is always important to know with precision the final composition/absorption in order to simplify kinetic equations.

In literature, a widely accepted actinometer for batch photoreactors is the Hatchard-Parker actinometer ($\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$) which produces Fe^{2+} in the presence of light. [22, 23] This actinometer is characterized by a high quantum yield (> 0.9) and is recommended by the IUPAC for accurate measurements. Nevertheless, in 2014 Aillet et al. reported difficulties encountered with this actinometer when performing measurements in flow

Fig.1 Sectional view of the Corning® Lab Photo Reactor

photoreactors. [8] Indeed, due to increased concentrations of ferrioxalate, necessary to reach full absorption, some precipitation phenomenon and clogging occurred in the studied microchannels. As a consequence, it appears necessary to evaluate other actinometers which are fully soluble in order to characterize microfluidic systems. In 2017, our team reported a facile procedure using azobenzene as a convenient actinometer at 365 nm in various solvents. [9] The main advantage of this procedure concerned the low cost of azobenzene and the use of NMR as a quantitative spectroscopic technique to simplify kinetic measurements. The same year, Roibu et al. reported the use of a diarylethene (DAE) for actinometric measurements in flow. [10] In their study, on-line UV–Vis characterization was performed for the kinetic monitoring. Both DAE [24] and azobenzene can be used at different wavelengths from UV [25] to visible range [13] and are good alternatives to Hatchard-Parker actinometer. In the present study, we were interested in demonstrating the applicability of our previously described method for the actinometric characterization of a commercially available flow photoreactor (Corning® Lab Photo Reactor) at 4 different wavelengths disposable in the apparatus (365, 385, 405 and 475 nm). Another key point of such fine characterization concerns its use for quantum yield determination and an example of such usage is described here to exemplify the robustness of the method.

2 Photokinetic model

The photokinetic model describing azobenzene $Z \leftrightarrow E$ photoisomerization has been introduced in 1957 by Zimmerman et al. whom used UV–visible spectroscopy for kinetic measurements. [25] Quantum yields for both processes can be determined with precisions from 5 to 10% over wide ranges of wavelength, concentrations and light intensities. The quantum yield depends only on the wavelength and is approximately constant throughout a single absorption band. Their results suggest that the isomerization takes place as an ordinary equilibrated reaction between two electronic excited states (E^* and Z^*) until a photostationary state is obtained.

Since the photostationary state composition depends on both ϵ_E and ϵ_Z , the nature of the excitation wavelength is determinant and the photo-product should be studied in the dark to avoid any post-modification of the ratios. Furthermore, the photoisomerization composition is also influenced by a thermal isomerization over time. At room temperature, this thermal isomerization is slow ($k_{\text{thermal}, 25^\circ\text{C}} = 3.5 \times 10^{-3} \text{ h}^{-1}$) and can be neglected if the reaction temperature is maintained at room temperature. As a consequence, if the temperature of the system is not controlled under high power illumination, the kinetic measurement will be greatly affected due to a considerable

Fig. 2 Photoisomerization of azobenzene

increase of the reaction temperature with time. In the Zimmerman's actinometric procedure, the use of UV–visible spectroscopy for kinetic measurement rendered the physical model more complex to establish, since both ϵ_E and ϵ_Z extinction coefficients were necessary for accurate calculation. In our case the use of NMR gives access to both Z and E isomers concentrations with a good level of precision over time. In a previous study [7] we demonstrated that the photokinetic model can be written as below as long as the absorption is below 1 and the absorbance variation (ΔA) low:

$$\frac{d[Z_{PSS} - Z]}{dt} = \frac{I_{\text{photon(transmitted)}} \times \ln 10 \Phi_{E \leftrightarrow Z}}{Z_{PSS}} [Z_{PSS} - Z], \quad (7)$$

where Z and Z_{PSS} are the concentration of Z isomer over time and at the photostationary state; $I_{\text{photon(transmitted)}}$ is the photon flux transmitted inside the reaction medium; Φ_E is the quantum yield for the $E \leftrightarrow Z$ photoisomerization (Fig. 2).

Fig. 3 Literature survey of measured azobenzene Φ_{EZ} quantum yields (representation of the averaged tendency vs. wavelength with averaged standard deviation in pink)

3 Results and discussion

3.1 Actinometry with azobenzene

3.1.1 Quantum yield usage and accuracy

A key point for these calculations is to work with correct quantum yields for which a slight variation can have a great influence on results. Since more than 50 years, a lot of quantum yields for azobenzene isomerization (Φ_{EZ}) had been described in the literature by different teams [13, 25–31]. A high deviation clearly appears for these different quantum yields values at a given wavelength (Fig. 3). In particular, in 2017, Heger team recalculated azobenzene quantum yields in methanol and values described are much higher than previously described values [31]. These data can be questionable if we pay attention to their extremely low sample standard deviation ($\leq 1\%$) which should be much higher ($\geq 2\%$ for older values) according to the accuracy of the instrumentation used and to the mathematical approximations necessarily (Taylor series expansions) introduced for such calculation.

As long as a high variability on the final result can be obtained by choosing one of these quantum yield values, we focus our study using appropriate and fixed values to fit with external radiometric measurements combined with the total internal light transmittance of the reactor. Moreover, thanks to this graphical representation, we were able to estimate unknown quantum yields of Azobenzene for 385 nm and 475 nm wavelength assuming an overall range of uncertainty ($\pm 3.5\%$).

3.1.2 Total transmittance model

To fit our quantum yields with the emitted power of each LEDs, total transmittance was determined for a given wavelength considering the refractive index n_g of the glass reactor (borosilicate, between 1.530 and 1.540 according to the wavelength), and the refractive index of air n_a (1.000), methanol n_m (1.326) and thermal fluid (water) n_w (1.000) which was used to maintain the temperature of the system. Transmittance without absorption was first calculated using Eq. 8 with reported values of refractive index under normal incidence light penetration:

$$T\%_{\text{(without absorption)}} = \left(1 - \left(\frac{n_a - n_g}{n_a + n_g}\right)^2\right) \times \left(1 - \left(\frac{n_g - n_w}{n_g + n_w}\right)^2\right) \times \left(1 - \left(\frac{n_g - n_w}{n_g + n_w}\right)^2\right) \times \left(1 - \left(\frac{n_g - n_m}{n_g + n_m}\right)^2\right). \quad (8)$$

To determine experimentally and precisely the total transmittance of the reactor, half of the photoreactor plate (same glasses including the thermal channel) was placed in front of the detector at the same distance than in the Corning® Lab Photo Reactor. For a good correlation, absorption of the glass reactor, methanol and the thermal fluid were also measured to calculate the final total transmittance (Table 1). Incident irradiance of the LEDs was also characterized using radiometric measurements at every wavelength (source light power setpoint = 20%).

3.1.3 Absorbed photon flux density

These data in hand, a concentrated solution of (*E*)-Azobenzene in methanol was injected into the Corning® Lab Photo Reactor at various flow rates and irradiated by either UV or visible LEDs at different wavelengths (365, 385, 405 and 475 nm) to establish the kinetic data at fixed

times. In order to obtain accurate actinometric measurements, the concentration of the solution was fixed in order to produce 99% of light absorption (nearly full absorption of emitted photons) according to Beer–Lambert Law and measured ϵ_E values at every studied wavelength. At the outlet, the solution was collected into the dark and monitored in a row by ^1H NMR or HPLC which gave similar results. The photostationary state of the azobenzene system is reached when the ratio of *E* and *Z* isomers is constant as a function of time (Fig. 4).

It is important to note that for some wavelengths (385, 405 and 485 nm), the photostationary state was accessed too

rapidly when the power of LED was high (> 30%). Consequently, the determination of kinetic constants was rendered uncertain due to less consistent data. Thus, to slow down the isomerization rate the light power setpoint was limited to 20%. Furthermore, since the rate of the photoreaction is proportional to the light power, any rate constant gives access to the LED irradiance at a defined light power by considering the transmittance of the system. To determine the photostationary state (Z_{PSS}), reactions were performed at long residence time using a high LED power value. Moreover, since the composition of the photostationary state depends on the wavelength, actinometric measurement can give information about the calibration of the irradiation source.

For each wavelength, the given data were then used to plot $\ln(Z_{\text{PSS}} - Z)$ vs. time which exhibits in each case an excellent squared correlation coefficient ($R^2 = 0.99$) (Fig. 5).

The absolute value of the slope for each graph gives the kinetic constant k which can be defined by Eq. 9 as

$$k = \frac{I_{\text{photon(transmitted)}} \ln 10 \Phi_E \epsilon_E}{Z_{\text{PSS}}}. \quad (9)$$

The quantum yield Φ_{EZ} and the molar extinction coefficient ϵ_E vary with the wavelength. The photostationary state composition (Z_{PSS}) and the (*E*)-Azobenzene molar extinction coefficient ϵ_E were redetermined for each wavelength using UV–Vis spectrophotometry at various concentrations in methanol (see ESI).

Thanks to the obtained k and Z_{PSS} , $I_{\text{photon}(\lambda)(\text{transmitted})}$ ($\text{ein.s}^{-1}.\text{cm}^{-2}$) has been calculated for a given wavelength and light source power. Finally, Q_{inside} (mW.m^{-2}) is obtained by multiplying $I_{\text{photon}(\lambda)(\text{transmitted})}$ by the energy of 1 mol of photons. In order to compare our experimental values to those given by the radiometer (see Table 2, Q_{Oemitted} measured in mW.cm^{-2}), the Q_{inside} value is divided by the total transmittance $T(\%)$ to give the total

Table 1 Total transmittance and radiometry measurements

Entry	Wavelength (nm)	Total transmittance ^a (%)	Incident irradiance ^b (mW.cm ⁻²)
1	365	71.7	15.2
2	385	71.7	15.4
3	405	75.8	16.4
4	475	75.5	9.2
5	610	78.0	7.4

^aDetermined using a Admesy Hera spectrometer (360–830 nm) located at 3.45 cm from the LEDs panel light source (operating at 20% light power setpoint) and behind a half Corning® Lab Photo Reactor plate.

^bMeasured at 3.45 cm from the LEDs panel light source using an Admesy Hera spectrometer (360–830 nm).

Fig. 4 Evolution of *E*-azobenzene and *Z*-azobenzene at 405 nm

Fig. 5 Graphs of $\ln(Z_{PSS} - Z_t)$ vs. time at various wavelengths

Table 2 Results of chemical actinometry assessment using (E)-azobenzene in Corning® Lab Photo Reactor

Entry	Wave-length (nm)	Z_{PSS}	Φ_{EZ}	ϵ_E^a (MeOH)	k ($10^{-2} \times s^{-1}$)	I_{Photon} ($10^{-4} \times \text{ein. s}^{-1} \cdot \text{m}^{-2}$)	Power (%)	$Q_{0emitted}$ calculated ^b (mW. cm^{-2})	$Q_{0emitted}$ measured ^c (mW. cm^{-2})
1	405	0.148	0.23	370	2.7	2.0	5	4	4.1
2	405	0.148	0.23	370	5.3	4.0	10	7.9	8.2
3	405 ^d	0.148	0.23	370	5.1	3.8	20	15.0	16.4
4	475	0.266	0.28	384	3.3	3.6	10	5.9	4.6
5	475 ^d	0.266	0.28	384	2.8	3.1	20	10.2	9.2
6	385	0.172	0.19	218	1.7	3.1	10	6.8	7.7
7	385 ^d	0.172	0.19	218	1.7	3.1	20	13.3	15.4
8	365	0.415	0.12	312	1.4	6.8	20	15.5	15.2

Kinetic studies at different wavelengths; concentrations were adjusted in accordance to an almost total absorbance (99%)

^aExtinction coefficient in $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ measured at 4 different concentrations

^bCalculated for one LEDs panel taking into account the total transmittance

^cMeasured at 3.45 cm of one LEDs panel (= distance from the center of the fluidic module)

^dWith only one LEDs panel switched ON over the two.

irradiance emitted by the light source at the external wall of the borosilicate reactor chip (see Table 2, $Q_{0emitted}$ calculated in $\text{mW} \cdot \text{cm}^{-2}$).

Table 2 includes all of the experimental data for the chemical actinometry study using the isomerization properties of (E)-azobenzene at four different wavelengths (365, 385, 405 and 475 nm). No data have been acquired at 610 nm since (E)-azobenzene does not absorb at this wavelength.

In order to neglect the thermal reverse isomerization, the photoreactor and the UV LEDs need to be thermoregulated. Additionally, as previously mentioned to obtain more accurate measurements low power should be applied. At 405, 475 and 385 nm, low light set power was applied (5–10%, Table 2, entries 1–2, 4, 6) to slow down the isomerization. Indeed, even at low power the LEDs panels installed into the Corning® Lab Photo Reactor deliver a very high photon flux which are much higher than the one delivered by conventional light sources (light bulbs or lamps). This criterion is important for productivity since the rate of any photoreaction is related to the rate of photon absorption (reaction characteristic) and to the amount of photons crossing the reaction medium (light source characteristic). For all these data, calculated $Q_{0emitted}$ values are close to the experimental values measured by radiometry confirming the accuracy of our photokinetic model for any wavelength. When only one LED panel at 385, 405 and 475 nm was used instead of two (entries 3, 5, 7), the value of k was divided by 2, which is in accord with a decrease by 2 of the light power. Note that the photon flux delivered at each wavelength is different with a similar applied light power. This is due to the different photoelectric properties of the LEDs materials. At 365 nm, the temperature control of the system is mandatory since the UV LED system transfers more heat to the photoreactor

device. Within these conditions (i.e. at 20% of light power), accurate measurement was obtained (entry 8).

Next, using the same methodology, we evaluated the linearity of the measured photon fluxes as a function of the applied LEDs sources power at various wavelengths (Fig. 6, Tables 3, 4, 5, 6). The power of the LEDs sources was varied from 5 to 60% and kinetics studies were performed to determinate k in order to obtain $I_{Photon(\lambda)(transmitted)}$ and then $Q_{0emitted}$ calculated for each wavelength. For this study, all samples are collected and handled using the same procedure as previously described and experiments are repeated three times using kinetic monitoring. For a fixed residence time of 16.2 s, the proportion of Z isomers (in %), k (s^{-1}), $I_{Photon(\lambda)(transmitted)}$ ($\text{ein} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$) and $Q_{0emitted}$ calculated ($\text{mW} \cdot \text{cm}^{-2}$) are reported in Tables 3, 4, 5, 6 ((365 nm), (385 nm), (405 nm) and 6 (475 nm), respectively). Due to high reproducibility of the method (see error bars on plots) for kinetic monitoring in the Corning® Lab Photo Reactor, this residence time as been selected since it corresponds to a time comprised between the initial time and the photostationary state for every studied photoisomerization reactions and a single point method could be extrapolated from this residence time by extracting the kinetic constant k according to an order 1 kinetic model. According to these data, it appears that the most powerful LEDs is obtained for the wavelength $\lambda = 405$ nm followed by $\lambda = 385$ nm, $\lambda = 365$ nm and finally $\lambda = 475$ nm.

By plotting I_{Photon} vs. light power (Fig. 6), excellent correlations ($R^2 \geq 0.98$) were obtained which means that the photon flux is proportional to the light power of every sources.

The $I_{Photon(\lambda)(transmitted)}$ received over the volume of the photoreactor ($I_{Photon(\lambda)(transmitted)}$ vol. in $\text{ein} \cdot \text{s}^{-1} \cdot \text{L}^{-1}$) could be easily converted by dividing the obtained $I_{Photon(transmitted)}$

Fig. 6 Variation of I_{photon} with applied LEDs light power (365, 385, 405, 475 nm)

Table 3 Results of chemical actinometry as a function of light power at 365 nm in Corning® Lab Photo Reactor

Entry	Light power (%)	%Z ^a	k (s ⁻¹)	I_{photon} (ein.s ⁻¹ .m ⁻²) ^b	Q_{emitted} ^c (mW.cm ⁻²)
1	5	2.4	3.7×10^{-3}	1.8×10^{-4}	4.1
2	10	4.3	6.8×10^{-3}	3.3×10^{-4}	7.4
3	20	8.1	1.3×10^{-2}	6.5×10^{-4}	14.8
4	30	11.1	1.9×10^{-2}	9.3×10^{-4}	21.1
5	40	14.2	2.6×10^{-2}	1.2×10^{-3}	28.6

^aMeasured by ^1H NMR at 10 mL.min⁻¹ (photoreaction time = 16.2 s); C = 0.08 M

^b $I_{\text{photon(transmitted) vol.}} = I_{\text{photon(transmitted)}}/l$ (with optical path = 0.04 cm)

^cCalculated by ^1H NMR for the 2 LEDs panels switched ON and taking account of total transmittance

Table 4 Results of chemical actinometry as a function of light power at 385 nm in Corning® Lab Photo Reactor

Entry	Light power (%)	%Z ^a	k (s ⁻¹)	I_{photon} (ein.s ⁻¹ .m ⁻²) ^b	Q_{emitted} ^c (mW.cm ⁻²)
1	5	2.3	8.9×10^{-3}	1.6×10^{-4}	3.5
2	10	4.2	1.7×10^{-2}	3.1×10^{-4}	6.8
3	20	7.6	3.6×10^{-2}	6.5×10^{-4}	14.1
4	30	9.8	5.2×10^{-2}	9.4×10^{-4}	20.4
5	50	12.9	8.6×10^{-2}	1.5×10^{-3}	33.4

^aMeasured by ^1H NMR at 10 mL.min⁻¹ (photoreaction time = 16.2 s), C = 0.11 M

^b $I_{\text{photon(transmitted) vol.}} = I_{\text{photon(transmitted)}}/l$ (with optical path = 0.04 cm)

^cCalculated by ^1H NMR for the 2 LEDs panels switched ON and taking account of total transmittance

received over the surface of the photoreactor by its optical path (0.04 cm). These data allowed us to completely characterize the Corning® Lab Photo Reactor and the 4 following equations can be used to estimate the photon flux density inside the reaction path in case of quantum yield determinations or for kinetics prediction:

$$365\text{nm} : I_{\text{photon(365)(transmitted)}} = 3.1 \times 10^{-5} \times \text{Light Power}_{(\%)}, \quad (10)$$

$$385\text{nm} : I_{\text{photon(385)(transmitted)}} = 3.6 \times 10^{-5} \times \text{Light Power}_{(\%)}, \quad (11)$$

$$405\text{nm} : I_{\text{photon(405)(transmitted)}} = 4.2 \times 10^{-5} \times \text{Light Power}_{(\%)}, \quad (12)$$

Table 5 Results of chemical actinometry as a function of light power at 405 nm in Corning® Lab Photo Reactor

Entry	Light power (%)	%Z ^a	k (s ⁻¹)	I _{photon} (ein.s ⁻¹ .m ⁻²)	Q _{emitted} ^c (mW.cm ⁻²)
1	10	8.8	5.5 × 10 ⁻²	4.2 × 10 ⁻⁴	8.2
2	20	12.3	1.1 × 10 ⁻¹	8.3 × 10 ⁻⁴	16.1
3	30	13.8	1.7 × 10 ⁻¹	1.2 × 10 ⁻³	24.4
4	40	14.4	2.2 × 10 ⁻¹	1.7 × 10 ⁻³	32.6

^aMeasured by ¹H NMR at 10 mL.min⁻¹ (photoreaction time = 16.2 s), C = 0.066 M;

^bI_{Photon(transmitted)} vol. = I_{Photon(transmitted)}/l (with optical path = 0.04 cm).

^cCalculated by ¹H NMR for the 2 LEDs panels switched ON and taking account of total transmittance.

Table 6 Results of chemical actinometry as a function of light power at 475 nm in Corning® Lab Photo Reactor

Entry	Light power (%)	%Z ^a	k (s ⁻¹)	I _{photon} (ein.s ⁻¹ .m ⁻²)	Q _{emitted} ^c (mW.cm ⁻²)
1	10	9.9	2.9 × 10 ⁻²	3.1 × 10 ⁻⁴	5.1
2	20	15.6	5.4 × 10 ⁻²	5.9 × 10 ⁻⁴	9.8
3	30	19.5	8.2 × 10 ⁻²	8.8 × 10 ⁻⁴	14.6
4	40	22.0	1.1 × 10 ⁻¹	1.1 × 10 ⁻³	19.3
5	60	24.6	1.6 × 10 ⁻¹	1.7 × 10 ⁻³	28.6

^aMeasured by ¹H NMR at 10 mL.min⁻¹ (photoreaction time = 16.2 s), C = 0.064 M

^bI_{Photon(transmitted)} vol. = I_{Photon(transmitted)}/l (with optical path = 0.04 cm)

^cCalculated by ¹H NMR for the 2 LEDs panels switched ON and taking account of total transmittance

$$475\text{nm} : I_{\text{Photon}(475)(\text{transmitted})} = 2.8 \times 10^{-5} \times \text{Light Power}_{(\%)} \quad (13)$$

3.2 Application to the determination of isatin N²-phenylhydrazones photoisomerization quantum yield by NMR

In order to demonstrate the applicability of such methodology for photokinetics studies within commercially available continuous flow photoreactor, we recalculate the known photochemical quantum yield of isatin N²-phenylhydrazones recently described in literature.

Indeed, in 2015 Cigáň et al. reported the Z ↔ E photoisomerization study of isatin N²-phenylhydrazones via UV–visible spectroscopy for which a very low quantum yield Φ_Z ≈ 1 × 10⁻³ was determined in batch (Fig. 7). [32] isatin N²-phenylhydrazones derivatives which are easily synthesized from isatin and phenylhydrazine present high photochromic properties at 405 nm, efficient reversible photoreaction and

Fig. 7 Photokinetics study of isatin N²-phenylhydrazone Z ↔ E isomerization at 405 nm

excellent thermal stability making them interesting alternatives to IUPAC recommended actinometers at this wavelength.

Considering these photoisomerization process, our photokinetic model developed for (E)-azobenzene photoisomerization could be applied to determine the photochemical quantum yield of isatin N²-phenylhydrazone. Taking into account the much smaller optical path in the Corning® Lab Photo Reactor (0.4 mm) and to handle sufficient quantities for ¹H NMR analysis, the concentration was increased up to 2 × 10⁻³ mol. L⁻¹. Under such concentration conditions the absorption is around 99% (ε_Z = 12,270 L.mol⁻¹.cm⁻¹) leading to a nearly total absorption of photons which allows very accurate measurements via NMR spectroscopy. In the Corning® Lab Photo Reactor the temperature can be maintained at 20 °C with an excellent heat removal, and consequently, the thermal isomerization can be neglected. The concentration of (Z)-isatin N²-diphenylhydrazones and (E)-isatin N²-phenylhydrazones can be easily quantified by ¹H NMR thanks to different shift of the E and Z isomers due to hydrogen bonding in the Z form. Photostationary state has been determined using a long residence time. The solution of (Z)-isatin N²-phenylhydrazones in methanol has been irradiated at 405 nm at various residence times with a light power of 100% (Fig. 8).

E_{PSS} (0.20) has been used as a parameter to plot the graph ln(E_{PSS} - E) vs. time which exhibits a linear relationship with an excellent squared correlation coefficient (R² = 1.00) (Fig. 8). The slope of the graph (0.070 s⁻¹) corresponds to

$$k = \frac{I_{\text{photon}(405)(\text{transmitted})} \ln 10 \Phi_Z \epsilon_Z}{E_{\text{PSS}}} \quad (14)$$

The quantum yield can be easily defined as

$$\phi_Z = \frac{k \times E_{\text{PSS}}}{I_{\text{Photon}(405)(\text{transmitted})} \times \ln 10 \times \epsilon_Z} \quad (15)$$

Substituting the values of E_{PSS} (0.2), k (0.07 s⁻¹), ε_Z (12,270 L.mol⁻¹.cm⁻¹) and I_{Photon(405)(transmitted)} (4.2 × 10⁻³ ein.s⁻¹.cm⁻²) which was previously determined (see Eq. 12)

Fig. 8 Photoisomerization of isatin N^2 -phenylhydrazone

affords $\Phi_Z (1.1 \times 10^{-3})$ which is in the same order of magnitude than the already described value in the literature. This method that provides the advantage of using rapid and quantitative ^1H NMR for monitoring the experiments instead of UV–visible spectrometry allows simplification of the mathematical treatment and measurements at higher concentrations closer to full photon absorption (99%) limiting by this way experimental approximations relative to absorption variations errors.

4 Experimental

4.1 Reagents and analysis

(*E*)-Azobenzene (98%) was purchased from TCI (TCI Europe N.V. Zwijndrecht, Belgium), isatin (98%) and phenylhydrazine (97%) were purchased from Sigma Aldrich (St. Louis, MO, USA), absolute ethanol (99.5%) was purchased from JT Baker Analysis (Phillipsburg, New Jersey, USA) and methanol (96.5%) was purchased for VWR Chemicals (Mouscron, Belgium), every chemicals were used as received. NMR spectra were recorded on a Bruker AVANCEIIIHD 300 spectrometer operating at ^1H = 300 MHz and ^{13}C = 75 MHz, equipped with a 5 mm

Fig. 9 View of the Corning® Lab Photo Reactor – Every tubing sections and the pumping modules are covered by aluminium foil to avoid any exposure to laboratory and natural external light

BBFO probe. Chemical shifts are given in parts per million relatives to solvent signal. Measurement of light source irradiance and estimation of total transmission of the reactor at various wavelengths according to both material absorption coefficients and refractive index parameters was performed with a Hera spectro-radiometer (Admesy®).

4.2 General procedure for the photoisomerization

Every connecting tubings from Lab Photo Reactor (Fig. 9) and round bottom flasks were covered with aluminium foil to avoid the exposure of the actinometer solution to the ambient light. A solution of (*E*)-Azobenzene at specified concentration (99% absorption in the system) in methanol was pumped through the photoreactor and irradiated at the desired wavelength (λ [concentration] in nm = 365[0.08 M], 385[0.11 M], 405[0.066 M] or 475[0.064 M]) at various flow rates (between 1 and 10 mL.min $^{-1}$). Light power of the LEDs was settled in a way that kinetics of the isomerization reaction can be observed over a larger period of time. The flow rates were chosen depending on the desired irradiation times ranging between 16 and 162 s. The first two cycles of irradiated solution were thrown away and the two second cycles were collected together in a round bottom flask. The solvent of irradiated samples was evaporated in the dark at 20 °C and the residue was then dissolved in 500 μL of CDCl_3 for analysis by ^1H NMR spectroscopy. The NMR tube was kept in the dark as long as possible before its introduction into the spectrometer. The degree of conversion was calculated by integrating the peaks that correspond to the (*Z*)-Azobenzene and to the (*E*)-Azobenzene isomers on the ^1H spectrum. The obtained results were then used to determine the photon flux inside the microreactor. Linearity of LEDs was verified using the same procedure except that flow rate and wavelength were constant and light power of LEDs was varied between 10 and 100%.

5 Conclusion

In conclusion we developed a multiple wavelength cheap and efficient chemical actinometry procedure based on photoisomerization of (*E*)-azobenzene under UV–visible light which could be easily implemented at an industrial level. Thanks to a quantum yield estimation and a rapid ^1H NMR analysis, results are very accurate for a variety of wavelengths from UV to visible range. Moreover, the determination of photon flux density transmitted in the photoreactor allowed us to verify the quantum yield of isatin *N*²-phenylhydrazone at 405 nm which validate our methodology. This result also demonstrates the possibility to realize precise photokinetics studies in a commercially available continuous flow photochemical reactor based on high power LEDs. This type of photoreactor allows to perform a large variety of reaction conditions via a modular interface thanks to a thermoregulated system. Since the procedure is safe and easy to implement, it will be extended to larger continuous photoreactor scale (e.g. Corning® G1 and G3) and could be used as routine analysis to characterize any Corning® Lab Photo Reactor for control and maintenance operations over time using the relevant data at the appropriate wavelength and temperature.

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Declarations

Conflict of interest There are no conflicts to declare.

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