



## Ferrioxalate actinometry with online spectrophotometric detection

Tímea Lehóczki, Éva Józsa, Katalin Ósz\*

Department of Physical Chemistry, University of Debrecen, Debrecen, Hungary

### ARTICLE INFO

#### Article history:

Received 20 August 2012

Received in revised form 2 October 2012

Accepted 6 October 2012

Available online 29 October 2012

#### Keywords:

Actinometry

Spectrophotometry

Photoreactor

### ABSTRACT

The best methods to study the stoichiometries of photochemical reactions are those that provide a continuous monitoring of the changes *e.g.* by measuring the spectral changes in the UV–vis region. Although the light of a diode array spectrophotometer or other lamp (UV lamp, LED, etc.) is not intense enough to generate the excited state in measurable quantities, it is enough to drive reactions, thus diode array spectrophotometers or LED-driven photoreactors with spectrophotometric detection are useful tools for these measurements. However, their illuminating light intensities need to be calibrated. The classical ferrioxalate actinometric method uses a separate complexation and spectrophotometric steps to determine the concentration of the Fe(II) formed during illumination. Decomposition of ferrioxalate is also accompanied by reproducible spectral changes, which are measured if the above mentioned techniques are used. This renders complexation and spectrophotometric Fe(II) concentration determination unnecessary. The present work introduces a simplified actinometric method, which was developed for photoreactors with spectrophotometric detection and used to calibrate such photoreactors with different arrangements. The method can be used for both polychromatic and monochromatic illuminating light sources. The relative error of the developed actinometric method is smaller than that of the classical actinometry.

© 2012 Elsevier B.V. All rights reserved.

### 1. Introduction

Ferrioxalate actinometry has been a standard tool of photochemical investigations for more than half a century now and is also recommended by IUPAC [1–5]. Its application usually involves the preparation of  $K_3[Fe(C_2O_4)_3]$  crystals, their dissolution in water, illumination and Fe(II) determination based on color formation with polypyridyl type ligands such as  $\alpha, \alpha'$ -dipyridyl or 1,10-phenanthroline. The monitored photoreaction involves the formation of Fe(II), carbon dioxide and free oxalate ion in a formal intracomplex electron transfer reaction. Standard values for the quantum yield of Fe(II) formation, and their wavelength dependence are known lending the method high adaptability. The useful wavelength range of the actinometric application (usually between 200 and 450 nm) is limited by the absorption characteristics of the complex.

In the past decade, diode array spectrophotometers have been increasingly used to study photochemical reactions in a highly quantitative manner [6–14]. The essence of this method is that diode array spectrophotometers have reasonably intense light sources, which can drive photochemical processes and detect them at the same time. No similar application of scanning spectrophotometers is possible as the light beams used in such instruments are

monochromatic and have low intensity. In fact, failure to recognize the mentioned characteristics of diode array spectrophotometers is a possible origin of confusing thermally activated and photochemical reactions [10,15,16].

Our group has recently reported an improvement of the photochemical use of diode array spectrophotometers by constructing a custom-built photoreactor using LED light sources and a fiber-optic CCD spectrophotometer as a detector [17]. This arrangement kept the advantageous online detection method possible in diode array spectrophotometers but decoupled the light beams used for illumination and detection. Therefore, the spectral properties of the driving light, which can only be changed by inserting filters in a diode array spectrophotometer, can be controlled by selecting appropriate LED light sources, which are available in a number of nearly monochromatic and also broad-spectrum varieties.

The illuminating light in these instruments is not powerful enough to generate excited state molecules in measurable quantities and, therefore, studying life times or other properties of these excited states is not possible with these techniques. Instead, the stoichiometric photochemical reactions are monitored [14]. In these techniques, light is considered as a reagent, whose amount and introduction into the system can be controlled in a much more sophisticated manner than the amounts of chemicals, or even flow rates.

Although the detectors in both diode array and CCD spectrophotometers typically support relative energy measurements as an option, it is still necessary to carry out actinometric measurements

\* Corresponding author. Tel.: +36 52 512900x22387; fax: +36 52 512915.  
E-mail address: [osz.katalin@science.unideb.hu](mailto:osz.katalin@science.unideb.hu) (K. Ósz).

in the two mentioned methods in order to determine the photon flux of the driving light beam and eventually to calculate quantum yields. In this process, we noticed that the UV–vis absorption of the illuminated ferrioxalate solution changes quite consistently. This observation opened a possibility to use this online absorbance signal for actinometric calculations. A successful development of this idea offers a greatly simplified procedure for actinometry, where the need for the separate Fe(II) analysis step with additional spectrophotometric measurements is eliminated. The present paper will report our results in method development based on these ideas.

## 2. Experimental

### 2.1. Materials

Potassium trisoxalatoferrate(III) trihydrate ( $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ ) crystals were prepared as described earlier [1].

For preparing and analyzing the actinometric test solutions, 1.0 M  $CH_3COONa$ , 0.50 and 0.050 M  $H_2SO_4$  stock solutions were also prepared. The concentrations of these solutions were checked by pH-potentiometric titrations.

Standard Fe(II) solutions of known concentration ( $3.4\text{--}3.7 \times 10^{-4}$  M) for calibration were prepared from Mohr's salt,  $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ , which was purchased from Sigma–Aldrich and used without further purification. The solution was kept in the dark after preparation. To avoid hydrolysis and oxidation of Fe(II), Mohr's salt was dissolved in 0.050 M  $H_2SO_4$  instead of water.

Solid  $\alpha, \alpha'$ -dipyridyl and 1,10-phenanthroline were purchased from Sigma–Aldrich and used as received to prepare stock solutions of known concentration (approximately 0.05 M). Dissolution of the ligands was accelerated by a sonicator.

All the solutions in this study were prepared in triply ion exchanged (Millipore) water.

### 2.2. Instrumentation

Two different types of instruments were used as photoreactors during the measurements. One was an AnalytikJena SPECORD S600 diode array spectrophotometer operating in the 190–1100 nm wavelength range with WinASPECT processing software and 60 ms integration time in most cases. The other was an Avantes Avaspec-2048 fiber-optic CCD spectrophotometer together with an Avantes AvaLight-DHc light source with a custom-built cell holder for photochemical measurements (this is called “photoreactor” in the further text). The detection-independent illuminating light sources in this constructed photoreactor were LEDs (Optosupply, cone angle of  $60^\circ$ ) emitting light of different wavelengths. The current passing through the LEDs (which determines the light intensity) was controlled by a variable resistor [17].

Furthermore, both the diode array spectrophotometers and the photoreactor were used with an additional high intensity Spectroline FC-100/F UV-A lamp [18] in the arrangement shown in Figure S1 in the supporting information. This lamp has a single emission line at around 365 nm and substantially higher photon flux than either the LEDs of the photoreactor or the lamps of the diode array spectrophotometer.

Standard quartz cells with 1.000-cm path lengths were used for the photochemical reactions. To obtain results suitable for quantitative comparison, the volume of irradiated samples was kept constant (2.50 mL) in the entire study. When the Spectroline FC-100/F UV-A lamp was used, the external light entered the sample from the top and the path length for that illumination was

2.50 cm. The same is also true for the LED light sources of the photoreactor.

The constant stirring necessary during the experiments was maintained using the built-in magnetic stirrer of the AnalytikJena diode array spectrophotometer or an additional LAB DISC magnetic stirrer (VWRI442-0745) and 7 mm teflon stirring rods for the photoreactor. The temperature was kept constant ( $25^\circ C$ ) using the built-in Peltier thermostat of the AnalytikJena diode array spectrophotometer or an outside thermostat for the photoreactor.

For standard actinometric measurements, a Shimadzu UV-1601 double beam scanning spectrophotometer working with UV Probe 2.21 software was used to measure the spectra of the Fe(II)- $\alpha, \alpha'$ -dipyridyl and -1,10-phenanthroline complexes and the concentration of Fe(II) formed during illumination was estimated based on the calibration. This instrument has a much lower light intensity compared to a diode array spectrophotometer, and normally cannot drive any photochemical reactions.

### 2.3. Iron(II) determination

For calibration, a working curve was recorded using the Fe(II) stock solution prepared from Mohr's salt and sulfuric acid solution. Two separate solutions containing the complexing ligands were also prepared ( $c_{\alpha, \alpha' \text{-dipyridyl}} = 0.0535$  M and  $c_{1,10\text{-phenanthroline}} = 0.0499$  M). Measured samples were prepared as follows: 10–650  $\mu L$  Fe(II) stock solution, 640–0  $\mu L$  water ( $V_{Fe(II)} \text{ stock solution} + V_{\text{water}} = 650 \mu L$ ), 25  $\mu L$  ligand stock solution, 1150  $\mu L$  sodium acetate solution (1.0 M), 750  $\mu L$   $H_2SO_4$  solution (0.50 M). The ligand/Fe(II) ratio was higher than 3 in all samples to ensure total complexation of the metal.

Figure S2 in the supporting information shows the molar absorption spectra of the complexes formed with the two different ligands. Based on these spectra, the Fe(II) concentrations of the actual samples were calculated from the absorbance values measured at 522 ( $\alpha, \alpha'$ -dipyridyl,  $\epsilon = 8538 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and 512 nm (1,10-phenanthroline,  $\epsilon = 10910 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), where the absorption maxima are located. Figures S3 and S4 in the supporting information show the calibration lines. Considerable deviation from the straight lines are detected at  $c_{Fe(II)} > 1.4 \times 10^{-4}$  M because the absorbance values measured are too high ( $>1.3$ ) to be measured accurately.

### 2.4. Standard actinometric measurements

Actinometric measurements were performed with standard ferrioxalate actinometry following literature recommendations [1–5]. For these measurements, 1–1.5 mg of solid  $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$  was measured directly into the cuvette and then dissolved in 2.50 mL of 0.050 M  $H_2SO_4$  solution and irradiated by the light source of choice.

The concentration of Fe(II) formed during the irradiation was measured using the following samples: 650  $\mu L$  of irradiated sample (containing ferrous ion), 26  $\mu L$  of 0.0535 M  $\alpha, \alpha'$ -bipyridyl solution, 1150  $\mu L$  of 1.0 M sodium acetate and 750  $\mu L$  of 0.50 M  $H_2SO_4$  solution (final pH: 5.1). The solution volumes were measured by an automatic pipette but their accuracy was also checked by measuring the weights of the solution components by an analytical balance. The analytical concentrations of the samples and also their total volumes were calculated using the mass measurement data, assuming a density of  $1.00 \text{ g cm}^{-3}$  for all components. For this concentration measurement, the Shimadzu UV-1601 double beam scanning spectrophotometer was used instead of the high light-intensity AnalytikJena diode array instrument.

Download English Version:

<https://daneshyari.com/en/article/26156>

Download Persian Version:

<https://daneshyari.com/article/26156>

[Daneshyari.com](https://daneshyari.com)