

## Short Communication

Azobenzene as a convenient actinometer: evaluation values for UV mercury lines and for the N<sub>2</sub> laser line

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## 1. Introduction

Photoreactions can be suitable for convenient and exact chemical actinometry if their rate law is easy to calculate and if the changes in concentration of the reaction products can be spectroscopically followed with time. This has been shown for the *trans-cis* photoisomerization of azobenzene. The following equation has been given [1]:

$$\int_{E_1}^{E_2} F(E') \frac{dE}{E - E_\infty} = -I_0 Q \int_{t_1}^{t_2} dt \quad (1)$$

where  $E$  is the absorbance at the wavelength of measurement,  $E_\infty$  is the related absorbance at infinite irradiation time (the photostationary state),  $E'$  is the absorbance at the irradiation wavelength,  $\epsilon'_A$  is the correlated absorptivity,  $F(E') = E'/(1 - e^{-E'})$  is the photokinetic factor,  $I_0$  is the irradiation intensity in einsteins per square centimetre per second,  $Q = 1000(\varphi_1^A \epsilon'_A + \varphi_2^B \epsilon'_B)$  is a pseudo quantum yield and  $\varphi_1^A$  is the partial photochemical quantum yield of the *trans-cis* step.

This equation can be solved using the method of "linear interpolation" [1, 2]:

$$I_0 = \frac{1}{-Q(t_1 - t_2)} \left\{ \frac{F(E'_1)(E_2 - E_\infty) - F(E'_2)(E_1 - E_\infty)}{E_2 - E_1} \ln \frac{E_1 - E_\infty}{E_2 - E_\infty} \right\} + F(E'_1) - F(E'_2) \quad (2)$$

To reduce experimental expenditure the measurement and irradiation wavelengths can be chosen to be the same ( $E = E'$  in eqn. (1)). Either the irradiation intensity  $I_0$  or the value of  $Q$  has to be known for the evaluation.  $Q$  has been obtained for a wavelength of 313 nm [1] using the ferric oxalate actinometer according to Hatchard and Parker [3, 4] and eqn. (1). We report

in this work determinations of the pseudo quantum yield  $Q$  for other mercury lines.

If the change in  $E'$  during the photoreaction is small (for the irradiation wavelengths 254, 280, 365, 405 and 436 nm), the exactness of the evaluation can be improved by measuring the absorbance both at the irradiation wavelength and at 313 nm where the absorbance changes significantly. Then  $E'$  is only used for the calculation of  $F(E')$  and the standard deviation of the  $Q$  value can be drastically improved. If the change in  $E'$  is very small ( $\Delta E' \approx 0.01$ ) between two supporting measurement points  $t_1$  and  $t_2$ , the evaluation becomes even simpler since eqn. (1) can be solved using the approximation

$$F(E') = \frac{F(E'_1) + F(E'_2)}{2} \quad (3)$$

in a closed form:

$$I_0 = \frac{1}{-Q(t_1 - t_2)} \frac{F(E'_1) + F(E'_2)}{2} \ln \frac{E_2 - E_\infty}{E_1 - E_\infty} \quad (4)$$

## 2. Results

Table 1 gives the  $Q$  values for some UV mercury lines [5] and the value for the  $N_2$  laser line (Molelectron) at 337.1 nm [6]. For the evaluations at 337.1 and 334 nm eqn. (1) was used under the condition  $E = E'$ . For the determination of the  $Q$  values for the 254, 405 and 436 nm lines the *cis-trans* back isomerization was followed, using preirradiated solutions as proposed previously [1, 7]. For the measurement of  $I_0$  at 436 nm a concentrated (0.15 M) ferric oxalate solution was used. The  $Q$  values of the 254 and 280 nm lines depend markedly on the mercury lamp used and on the interference filter, since the intensities (lines and continuum) of a mercury lamp in the range 250 - 290 nm are relatively high compared with the 254 and 280 nm lines themselves. These  $Q$  values should be determined in each laboratory for the specific lamp-filter combination.

Azobenzene proved to be very convenient in the  $N_2$  laser system when compared with the ferric oxalate method. All problems arising from actinometry by physical means could also be avoided [8]. Actinometry by azo-

TABLE 1

| Irradiation wavelength (nm) | $Q$ ( $\text{cm}^2 \text{mol}^{-1}$ ) |
|-----------------------------|---------------------------------------|
| 254                         | $(2.6 \pm 0.05) \times 10^6$          |
| 280                         | $(2.7 \pm 0.2) \times 10^6$           |
| 313                         | $(3.7 \pm 0.04) \times 10^6$          |
| 334                         | $(2.8 \pm 0.05) \times 10^6$          |
| 337.1                       | $(2.8 \pm 0.1) \times 10^6$           |
| 365/366                     | $(1.3 \pm 0.1) \times 10^5$           |
| 405/408                     | $(5.3 \pm 0.1) \times 10^5$           |
| 436                         | $(8.2 \pm 0.1) \times 10^5$           |

benzene becomes especially recommendable if a modern UV spectrometer, or even a combined irradiation and measurement apparatus [9], can be used which is preferable in photokinetics.

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