

CHEMICAL ACTINOMETRY IN THE UV BY AZOBENZENE IN CONCENTRATED SOLUTION: A CONVENIENT METHOD

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Summary

The advantages of concentrated solutions of azobenzene in actinometry are discussed. The experimental procedure and the correct method of evaluation are given in detail. The partial photochemical quantum yields for both photoisomerization steps were calculated by means of kinetic simulation and were checked using liquid chromatography. They differ for the π,π^* and the n,π^* transitions.

1. Introduction

Azobenzene has been recommended as a chemical actinometer in the UV and the visible irradiation range for several years [1 - 3]. Its use in dilute methanolic solution makes the evaluation time consuming. However, this method has the advantage that results can be obtained during the measurement procedure by using favourable photometric methods at a number of irradiation times. Therefore the actinometric system is exact, the measurement is straightforward and the evaluation is simple and quick if a personal computer is used. The method gives a number of intensity values which make it possible to check the stability of the light source and the measurement errors.

The advantages of using azobenzene as an actinometer are as follows. The mechanism of the photoreaction is simple and uniform. It is a trans-cis, cis-trans photoisomerization in which the thermal reaction steps can be neglected. The absorption spectra of the trans and cis compound differ enough to produce significant changes in the absorbances during the photoreaction; therefore photometric observation is favourable. The actinometer material is inexpensive, thermally stable, easily available and reusable because of the reversibility of the photoisomerization reaction.

The only disadvantage is the rather sophisticated evaluation procedure. To reduce the problem caused by the kinetic evaluation method [4] we report the use of a concentrated azobenzene solution (more than 6×10^{-4} M) which totally absorbs the irradiation to be measured but can be

photometrically followed and easily evaluated. Therefore the system combines the advantage of simple evaluation with the benefit of photometry and multiple observation during the irradiation procedure.

2. Photokinetic principles

The photoisomerization of azobenzene consists of two linearly dependent reaction steps. Therefore the following equation for simple uniform photoreactions is valid [2, 5]:

$$\frac{dE}{dt} = QI(E - E_{\infty}) \frac{1 - 10^{-E'}}{E'} \quad (1)$$

where the absorbances E and E_{∞} at the observation wavelength refer to times t and $t = \infty$ (photostationary state). E' is the absorbance at the irradiation wavelength, $I = 1000I_0$ is the intensity of irradiation in einsteins per square centimetre per second and Q is the pseudophotochemical quantum yield which is given by

$$\begin{aligned} Q &= R_1 + R_2 \\ &= \varphi_1^A \epsilon'_A + \varphi_2^B \epsilon'_B \end{aligned} \quad (2)$$

where $\epsilon'_{A, B}$ are the absorptivities at the irradiation wavelength and φ_1^A and φ_2^B are the partial quantum yields of the linearly dependent isomerization steps. The Q values for the UV mercury lines and the nitrogen laser line are available in the literature [2]. They were obtained by comparing azobenzene and ferrioxalate actinometers [6].

They can also be used to evaluate the concentrated solution. In the case when total absorption at the irradiation wavelength is assumed and the irradiation intervals are short, the change in the photokinetic factor $(1 - 10^{-E'})/E'$ will be very small and can be approximated by a mean value $(E')^{-1}$. When this assumption is made eqn. (1) can be integrated to give

$$\ln(E - E_{\infty}) = \ln(E_0 - E_{\infty}) - QI(\overline{E'})^{-1}t \quad (3)$$

Despite this simple relationship the evaluation of this equation is difficult since the determination of E' and E_{∞} is non-trivial and both isomers absorb in the whole range of irradiation wavelengths. Therefore a further assumption is made. The photoreaction is carried out only up to a turnover of 5%. In this case the error is limited by assuming that the absorption of the photoproduct is negligible and the photochemical back reaction need not be taken into account. Under these conditions eqn. (1) reduces to

$$I_0 = \frac{\Delta E}{1000} \varphi_1^A \epsilon_A \Delta t = W \frac{\Delta E}{\Delta t} \quad (4)$$

and a linear relationship between the measured change in the absorbance per unit irradiation time and the intensity of the irradiation source is obtained.

W depends on the measurement and irradiation wavelengths. Because of the approximation of total absorption and the assumption of a considerable difference between the absorptivities, the range of irradiation is limited to wavelengths between 254 and 334 nm at a concentration of 6×10^{-4} mol l⁻¹.

3. Results

The Q values were obtained by kinetic analysis in dilute solutions and ferrioxalate actinometry [2]. They were checked by calculation using eqn. (2) from the partial quantum yields and the molar absorptivities of the trans and cis compounds which were separated by liquid chromatography [7]. When the absorptivities are known the quantum yields can be calculated using the following relationship:

$$\frac{a_{\infty}}{b_{\infty}} = \frac{\epsilon'_B \varphi_2^B}{\epsilon'_A \varphi_1^A} \quad (5)$$

where a_{∞} and b_{∞} are the concentrations of the two components in the photostationary state. These concentrations can be calculated via the absorbance E_{∞} in the photostationary state and the total concentration a_0 of azobenzene according to the equations

$$a_{\infty} = \frac{E_{\infty} - \epsilon_B a_0}{d(\epsilon_A - \epsilon_B)} \quad (6)$$

and

$$b_{\infty} = a_0 - a_{\infty} \quad (7)$$

where a_0 is determined by measuring the absorbance at the isosbestic point $\lambda_{iso} = 268$ nm ($\epsilon_{iso} = 4460$ l mol⁻¹ cm⁻¹). The absorptivities, the partial quantum yields and the pseudoquantum yields are given for the mercury lines in Table 1. The partial photochemical quantum yields in the π, π^* and the n, π^* transition bands differ in agreement with the literature [8-10].

TABLE 1

λ' (nm)	ϵ_A (l mol ⁻¹ cm ⁻¹)	ϵ_B (l mol ⁻¹ cm ⁻¹)	φ_1^A	φ_2^B	Q_{exp}	Q_{calc}
254	2450	6900	0.26 + 0.02	0.31 + 0.02	$(2.75 + 0.05) \times 10^3$	2.78×10^3
280	8200	5200	0.12 + 0.02	0.34 + 0.02	$(2.7 + 0.2) \times 10^3$	2.75×10^3
313	22020	2940	0.13 + 0.005	0.30 + 0.03	$(3.7 + 0.05) \times 10^3$	3.74×10^3
334	16980	1100	0.15 + 0.02	0.30 + 0.03	$(2.8 + 0.05) \times 10^3$	2.88×10^3
365	360	190	0.15 + 0.03	0.35 + 0.03	$(1.3 + 0.1) \times 10^2$	1.21×10^2
405	305	840	0.20 + 0.02	0.57 + 0.03	$(5.3 + 0.1) \times 10^2$	5.4×10^2
436	490	1140	0.22 + 0.03	0.63 + 0.05	$(8.2 + 0.1) \times 10^2$	8.26×10^2

The values obtained for φ_1^A and φ_2^B are a good fit to the solvent dependence curve shown in ref. 9. The values within one absorption band are independent of wavelength. At an irradiation wavelength of 254 nm the partial quantum yields of the two steps differ by slightly more than the standard deviation whereas at longer irradiation wavelengths the *cis* \rightarrow *trans* yields are larger by factors of 2 and 3 respectively. The experimental and calculated Q values are in good agreement.

For a concentrated solution (6.4×10^{-4} M) of azobenzene in methanol a suitable observation wavelength is $\lambda = 358$ nm. At this measurement wavelength the values of W for the mercury lines at 254, 280, 313 and 334 nm are determined using a ferrioxalate actinometer [6, 7] and by comparison with the azobenzene actinometer in dilute solution [2, 3] (Table 2). The good agreement of the experimental results confirms the significance of actinometric measurements using the concentrated azobenzene solution. This new actinometer combines the advantages of a simple evaluation method because of total absorption with a simple photometric measurement procedure.

The absorbance at $\lambda = 358$ nm is measured before and during irradiation at wavelengths between 254 and 334 nm. The linearity of the absorbance-time diagram is demonstrated during several irradiation periods. The irradiation intensity is calculated from the slope of the $E-t$ diagram using eqn. (4). For actinometry of the 254 nm mercury line the azobenzene solution has to be pre-irradiated at $\lambda' = 313$ nm up to the photostationary state. The back irradiation at $\lambda' = 254$ nm can then be monitored.

TABLE 2

λ' (nm)	W (einsteins cm^{-2})
254	2.3×10^{-6}
280	4.6×10^{-6}
313	5.3×10^{-6}
334	3.6×10^{-6}

4. Experimental details

The separation of *trans*- and *cis*-azobenzene by liquid chromatography [11, 12] was carried out using light petrol ($50^\circ - 70^\circ$) and ethanol. The *cis* compound was dried using sodium sulphate and was evaporated and recrystallized from methanol. The crystalline material was weighed in for various concentrations to measure the absorbances and to determine the absorptivities of *cis*-azobenzene. All procedures were carried out under a red safety light.

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