

AZOBENZENE AS A CONVENIENT ACTINOMETER FOR THE DETERMINATION OF QUANTUM YIELDS OF PHOTOREACTIONS*

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Summary

Using u.v. spectroscopic measurements for the determination of the change in concentration of products, photoreactions can be employed as simple and convenient actinometers, if their photokinetic rate equations can be solved with sufficient accuracy. By application of the new "linear interpolation method" [4] this can be done for the photoisomerization of azobenzene in methanol as accurately as required with comparatively less mathematical expenditure and smaller errors than before. It is shown that this photoreaction fulfils the above requirements. Two different types of evaluation, an arithmetical and a graphical one, are compared. Their results and advantages are discussed.

Introduction

A photoreaction should be suitable for a convenient and exact chemical actinometer, if its rate law is easy to calculate and if the time-dependent change of the concentration of products can be measured in a simple way with high accuracy. These requirements could be met by measuring the absorbance change during reaction procedure, *e.g.* by spectroscopic means, for a non-complex and uniform photoreaction with well determined quantum yield. However, even for a very simple photoreaction, the exact rate equation normally cannot be solved by direct integration [1], since the factor:

$$F(E') = E' / (1 - 10^{-E'}) \quad (1)$$

which is part of every photokinetic rate law, is dependent on reaction time in most cases. According to the Lambert-Beer law, E' , the absorbance at the wavelength of irradiation, is given by all products of the solution, absorbing at this wavelength. Up to now the necessary approximations for $F(E')$ were either simple in calculation but very insufficient or caused extensive calculations [1 - 4]. Recently a new approximation method has been developed [4].

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By this method the factor $F(E')$ can be calculated for an absorbance E at the reaction time t between two supporting points of absorbance E_1 and E_2 at reaction times t_1 and t_2 by the following equation without large expenditure:

$$F(E) = \frac{F(E_1) \cdot E_2 - F(E_2) \cdot E_1}{E_2 - E_1} + E \left[\frac{F(E_2) - F(E_1)}{E_2 - E_1} \right] \quad (2)$$

By this so-called "linear interpolation" [4] the evaluation of spectroscopic measurements becomes unlimitedly exact using suitable supporting points. Since this method can be principally used for all photoreactions, a possibility was given, to obtain the rate of a photoreaction with required high accuracy and comparably low expenditure of calculation. It was necessary to test the procedure for a simple photoreaction; but only a very few of them are known. Thus the photoisomerization of azobenzene in methanol was chosen as a test system, since it has been examined in great detail [3, 5, 6] and has even been proposed as an actinometer [7].

Derivations

With the assumptions, that the irradiation is monochromatic, the quantum yields are independent on light intensity, and that the thermal *cis* → *trans* reaction is comparatively slower than the photoisomerization, the following rate law can be derived (for further details see ref. [1])

$$\frac{da}{dt} = \dot{a} = 1000 \cdot I_0 \cdot (\Phi_2^{cis} \cdot \epsilon'_{cis} \cdot b - \Phi_1^{trans} \cdot \epsilon'_{trans} \cdot a) [F(E')]^{-1} \quad (3)$$

where a and b are the concentrations of *trans*- and *cis*- azobenzene dependent on reaction time, I_0 is the intensity of irradiation, Φ_1^{trans} is the quantum yield for the first reaction step, whereby the photoreaction is initiated by the *trans*-product, Φ_2^{cis} is the corresponding quantum yield for the *cis*-*trans* photoreaction, and ϵ' is the molar absorbance coefficient at the irradiation wavelength.

With

$$a_0 = a + b \quad (4)$$

that means the *trans*-concentration at the beginning of the reaction equals the sum of the *trans*- and *cis*-products at any reaction time, and the condition $\dot{a} = 0$ in the photostationary state at time $t = \infty$,

$$a_\infty = \frac{\Phi_2^{cis} \cdot \epsilon'_{cis} \cdot a_0}{\Phi_1^{trans} \cdot \epsilon'_{trans} + \Phi_2^{cis} \cdot \epsilon'_{cis}} \quad (5)$$

is obtained. These equations give the time dependence of *trans*-azobenzene concentration to:

$$\dot{a} = - I_0 \cdot 1000 \cdot \underbrace{(\Phi_1^{trans} \cdot \epsilon'_{trans} + \Phi_2^{cis} \cdot \epsilon'_{cis})}_Q \cdot (a - a_\infty) [F(E')]^{-1} \quad (6)$$

The "pseudo total quantum yield" Q is independent of time and concentration. Because of the factor $F(E')$, the above equation cannot be solved by direct integration. Since it was proposed for an easy actinometer to measure the concentration change by spectroscopic means, eqn. (6) is altered by the following relations:

$$(a - a_{\infty}) = - \frac{(E - E_{\infty})}{q} \quad (7a)$$

and

$$\dot{a} = - \frac{\dot{E}}{q} \quad (7b)$$

according to ref. [1] with:

$$q = d (\epsilon_{cis} - \epsilon_{trans}) \quad (8)$$

According to eqn. (8), q is a time independent constant given by the optical pathlength and the molar absorbance coefficients. Thus the following equation is obtained from eqn. (6):

$$\int_{E_1}^{E_2} F(E') \frac{dE}{E - E_{\infty}} = - I_0 \cdot Q \cdot \int_{t_1}^{t_2} dt \quad (9)$$

By using the above mentioned "linear interpolation" method (eqn. 2), this integral can be solved with a systematic error smaller than 0.2%, even if the supporting points are as far apart as 0.2 absorbance units in the measurable region of absorbances $0.3 < E < 1.5$. The advantage is that neither total absorbance ($E' > 4$) nor negligible absorbance ($E' < 0.02$) at the irradiation wavelength is necessary to avoid the large errors (sometimes up to 40%) by the commonly employed approximations (see for references in refs. [1] and [4]). Therefore the irradiation wavelength and the wavelength for the "concentration"-measurement can be the same. The experimental procedure can be simplified to a large extent and in the following there is no reason to distinguish between E' and E . With this simplification and the above equations one gets the following expression for the light intensity, which can easily be calculated with any modern small calculator and fulfils the stated requirements for a convenient actinometer.

$$I_0 = - \frac{1}{Q(t_1 - t_2)} \left\{ \left[\frac{F(E_1)(E_2 - E_{\infty}) - F(E_2)(E_1 - E_{\infty})}{E_2 - E_1} \ln \frac{E_1 - E_{\infty}}{E_2 - E_{\infty}} \right] + F(E_1) - F(E_2) \right\} \quad (10)$$

Results

The intensity of the irradiation source has been determined for many different intensities by a large number of independent measurements accord-

ing to Parker [8, 9] for 313 nm. With this known intensity a mean value for the "pseudo total quantum yield" Q was calculated according to eqn. (10). This value proved to be independent on azobenzene concentration; its error depends mainly on the accuracy of the actinometry according to Parker. The value $Q = (3.70 \pm 0.05) \times 10^6 \text{ cm}^2/\text{mol}$ was obtained under our laboratory conditions. For routine application of this azobenzene actinometer two possibilities of evaluation are shown, an arithmetical and a graphical one.

Arithmetical method

To calculate eqn. (10) in an easy way, an HP-computer 9820 with peripheral apparatus was programmed*. In combined irradiation- and measuring-devices (single beam apparatus [10] and double beam recording system [11]) the absorbances at the irradiation wavelength were measured at certain reaction times t (the program also allows the calculation of intensities, if irradiation and measuring wavelength are different). In Table 1 a teletype print-out is given for one of those experiments. On top of the scheme the constant Q , the value E_∞ [$E(\text{UNEND})$], the number of measured absorbances, according to the number of supporting points for the "linear interpolation", and the choice of wavelength are printed out. Next, the values of $F(E)$ are calculated for the measured absorbances. Besides the reaction times, These absorbances are printed in the first row and second column, representing the supporting points E_1 and E_2 . The calculated intensities I_0 for any combination of these values E_1 and E_2 are given in a matrix-like representation, where the first value ($4.807E - 10$) results between $E_1 = 0.827$ and $E_2 = 0.734$, and the value $4.854E - 10$) between $E_1 = 0.827$ and $E_2 = 0.342$. This intensity has the largest systematic error, since the distance between the supporting points is the furthest, increasing in the first column from top to bottom and in the last row from right to left. On the other hand, the intensities with the smallest systematic error (calculated for the closest supporting points) are on the first diagonal (labelled with ① in Table 1); they give the mean intensity I_0 of the irradiation lamp in Einstein/cm²s. If they differ systematically, then the lamp intensity was not constant during measuring time. An inaccurate measurement of absorbance (error $\geq \pm 0.002$ absorbance units) can be detected very easily, e.g. the value 0.473 in the fifth row of the given example.

Further advantages of this arithmetical evaluation method are, that the value E_∞ does not have to be measured; it can be determined from a linear relationship between E_∞ and the absorbance at the isosbestic point. Inaccuracies in the determination of E_∞ can be detected very easily, since the matrix representation becomes inconsistent (mean values must increase slightly from ① to ⑤). Moreover, the knowledge of weight-in concentration is superfluous, only a good spectroscopically measuring region should be chosen. Further, it should be pointed out, that the knowledge of absorbance coefficients according to eqn. (10) is not necessary any more [7]. It turns out to

* This program, IØ-PRØG, can be obtained on request.

TABLE 1

Output of program IØ-PRØG. for different combinations of supporting absorbances and calculated mean intensities

KONST. Q = 3.700E 06

E(UNEND) = 0.236

MP-NUMB. = 7

ERR=MESS = 0

T(SEK)	F(E)	0.972	0.900	0.837	0.768	0.713	0.671	0.628
E'	E	0.827	0.734	0.650	0.553	0.473	0.410	0.342
ED		-0.093	-0.084	-0.097	-0.080	-0.063	-0.068	
0	0.827							
90	0.734	$4.807E-10^*$						
180	0.650	$4.814E-10$	$4.814E-10$					
300	0.553	$4.822E-10$	$4.820E-10$	$4.817E-10$				
420	0.473	$4.839E-10$	$4.835E-10$	$4.833E-10$	$4.841E-10$			
540	0.410	$4.844E-10$	$4.837E-10$	$4.831E-10$	$4.828E-10$	$4.808E-10$		
720	0.342	$4.854E-10$	$4.845E-10$	$4.837E-10$	$4.830E-10$	$4.817E-10$	$4.819E-10$	

Calculated intensity for diagonal with mean value in $[\times 10^{10}$ Einstein/cm² s]

- ① 4.82 ± 0.02
- ② 4.82 ± 0.01
- ③ 4.83 ± 0.01
- ④ 4.84 ± 0.01
- ⑤ 4.84 ± 0.01

*Three digits behind the decimal point are only used for arithmetic reasons. Irradiation and measured wavelength was 313 nm.

be unnecessary to take a larger number of supporting points (absorbance change $ED < 0.1$), since the error caused by the approximation of linear interpolation, is far less than the obtainable accuracy of absorbance measurements.

Graphical method

In case the convenient possibility of a small computer is not given, the following procedure might be favoured. In a test measurement (for this case the above values were used) the absorbance as dependent on reaction time is plotted against τ values, which are calculated from the relation:

$$\tau = I_0 Q t \quad (11)$$

t being the reaction time. This is done for a definite and chosen weight-in concentration. For all the following routine actinometric measurements it has to be determined at this concentration, defined by the absorbance at the isosbestic point. For those experiments the above test diagram is taken (curve in Fig. 1). The absorbance values, measured during the actinometric reaction, are marked on this test curve (in Fig. 1 by the numbers 1 to 6; the values of E taken for a different experiment, but with the same weight-in concentration as the test measurement). Next the origin of the τ axis is shifted parallel into the first measured absorbance value, marked in the test curve. Thus a τ value can be determined for each absorbance graphically on the new τ axis (- - -) and an intensity can be calculated from the related reaction time t and eqn. (11). The error depends on the accuracy of the test diagram and on the graphical representation.

Discussion

Azobenzene is shown to be the postulated convenient actinometer, since the experimental procedure is little, the same set-up and measuring technique as in photokinetics can be used, and the results are very good. For the measured light intensities [10^{-10} Einstein/s cm^2 for a HPK-125 (Phillips-high-pressure Hg lamps) or St 75 (Hanau high-pressure Hg lamp)] the thermal *cis-trans* isomerization is incomparably slower. The absorbance change is 0.005 in 1 h, whereas the photoreaction results in the change of 0.1 absorbance units in a few minutes. The advantages of this new method are:

- (1). There is no need for extensive sample preparation under specific conditions.
- (2). The reaction is insensitive to oxygen.
- (3). The knowledge of the molar absorbance coefficients of the *cis*- and *trans*-product is not necessary any more.
- (4). Only during the actinometric irradiation itself, does stray light have to be avoided; light, which falls on the cell before the actual actinometric measurement, does not influence the results at all.
- (5). With a few values of absorbance only, even taken just at one wavelength, several intensity values are obtained for each experiment; from those the average can be taken.

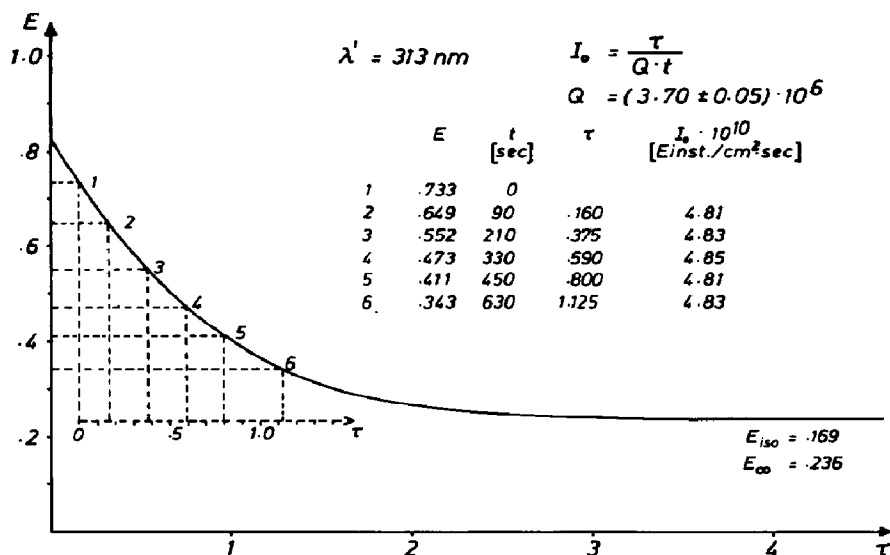


Fig. 1. Test diagram for actinometric measurement of azobenzene in methanol; irradiation and absorbance measurement wavelength, 313 nm.

(6). In the case of the arithmetical evaluation the knowledge of weight-concentration is not necessary at all; with less arithmetical expenditure the graphical method needs a definite concentration, which can be "weight-in" by means of the isosbestic point.

The photoisomerization of azobenzene can be used directly in the region of ~ 365 to 268 nm. For an irradiation wavelength below 268 nm, at first the *cis*-product has to be produced by irradiation at longer wavelength. Then the photoreaction of the *cis*-azobenzene could be used for actinometric purposes [7].

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