Short Communication

A convenient actinometer for the determination of irradiation intensities at 350 - 390 nm

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(Received January 31, 1977)

In cases where photokinetic rate equations can be solved with sufficient accuracy and the change in concentration of the products can be determined by UV spectroscopic measurements, photoreactions could be employed as simple and convenient actinometers. This has been shown for azobenzene [1]. An even more convenient procedure to determine the intensity of an irradiation source in the wavelength range 350 - 390 nm using another evaluation method is proposed.

For a simple photoreaction [2] such as B $\xrightarrow{h\nu}$ C the following equation is valid:

$$\dot{b} = \frac{-1000 I_0 \mathcal{H}_B b \phi^B (1 - e^{-A})}{A} \tag{1}$$

where the wavelength of irradiation with intensity I_0 and the wavelength for observation of the change b of concentration are the same, A is the natural absorbance, $\mathcal{H}_B$ is the natural molar absorption coefficient of the reactant B and ϕ^B is the photochemical quantum yield. The equation can be simplified and solved by assuming that at the irradiation wavelength only the reactant B absorbs.

Using a cell path length of 1 cm and substituting $A = \mathcal{H}_B b$ and $\dot{A} = \mathcal{H}_B \dot{b}$ in eqn. (1) the following relationship is obtained:

$$\dot{A} = \frac{-1000 I_0 \mathcal{H}_B A \phi^B (1 - e^{-A})}{A} \tag{1a}$$

Integration between the time limits t and $t = 0$ gives in decadic units of absorptivity

$$\ln (10^A - 1) = \ln (10^{A_0} - 1) - 1000 I_0 \phi^B \times 2.303 t \mathcal{H}_B \tag{2}$$

where A_0 is the absorbance at the start of the reaction. The above assumptions can be made for 2,2',4,4'-tetra-isopropylazobenzene [3] which shows a uniform photoisomerization. The graph of $\ln (10^A - 1)$ *versus* reaction time t is initially a straight line, but divergence from this linear relationship starts when the absorbance at the irradiation wavelength approaches zero. The constant for

the backward dark *cis–trans* isomerization was determined to be $k = (1.52 \pm 0.05) \times 10^{-5}\,\text{s}^{-1}$ at room temperature. The error caused by the dark reaction is negligible in the irradiation intensity range of the standard mercury lamps used (5×10^{-10} - 1×10^{-8} einstein $\text{cm}^{-2}\,\text{s}^{-1}$). Knowing the slope m of the graph the irradiation intensity can be determined. The photochemical quantum yield of the *trans–cis* photoreaction was calculated from a number of test measurements using the Parker actinometer [4] to be

$$\phi^B = 0.112 \pm 0.04$$

where errors in the determination of the absorption coefficients $\mathscr{K}_B = 19\,200$ at 365 nm and in the actinometry are included. This value was checked with the result of an extensive kinetic analysis [5] and shown to be correct within the error limits. Thus the irradiation intensity is given by

$$I_0 = -\frac{m(\text{s}^{-1})}{\phi^B 1000 \times 2.303\,\mathscr{K}_B} = -\frac{m}{(4.95 \pm 0.19) \times 10^6}\ \text{einstein cm}^{-2}\,\text{s}^{-1}$$

for an irradiation at 365 nm. The intensity required can easily be calculated from the slope of the simple graph by measuring a few absorbances during irradiation of the actinometric photoreaction. The advantages of this azobenzene derivative as an actinometer are as follows.

(1) There is no need for extensive sample preparation before actinometric measurement.

(2) The reaction is insensitive to oxygen.

(3) Light incident on the cell before or after the actual measurement does not influence the result.

(4) The results can easily be obtained immediately after the measurement.

Experimental

Solutions (10^{-5} M) of 2,2',4,4' -tetra-isopropylazobenzene in n-heptane (Merck Uvasol) were irradiated with a stabilized St-75-Hg-lamp (Quarzlampengesellschaft Hanau) and a Schott UV-Pil 365 nm interference filter at 20 °C. The solutions were stirred continually during irradiation. The experiments were run at temperatures from 20 to 30 °C and for light intensities from 5×10^{-10} to 1×10^{-8} einstein $\text{cm}^{-2}\,\text{s}^{-1}$ in cells of path length 1 cm. For all these conditions the results were within the error limits. The measurement and irradiation devices were a modified Zeiss PMQ II [6] or a DMR 21 system [7].

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