# PHOTOCHEMISTRY OF ADSORBED MOLECULES III: QUANTUM YIELDS OF PHOTOPROCESSES OF MOLECULES IN THE ADSORBED STATE

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## Summary

A method is described which allows the quantum yields of photoreactions of adsorbed molecules to be determined. This method is based on the solution of the kinetic equations for viscous media and the measuring of the optical density of the sample by means of an immersion technique. The quantum yields of the photoreactions can then be determined by fitting the calculated time dependence of the optical density $D(t)$ to the measured curve $D(t)$ *versus* $t$. The quantum yields of the photoisomerization of 1-(9-anthryl)-4,4-diphenyl-2,3-diazabutadiene adsorbed on silica gel were calculated by the method presented in this work.


## 1. Introduction

Reference should be made to Part II [1]. Investigations of photoprocesses in adsorbed molecules are important for understanding environmental effects on photophysical and photochemical processes in excited molecules. They are of special interest in photosynthesis, in photographic and photo-imaging systems, in the conversion of solar energy to chemical energy and for upper atmosphere chemistry.

Unfortunately only a small amount of quantitative kinetic data for light-induced processes in adsorbed molecules is available [2 - 5]. This is apparently because of some procedural difficulties in the investigation of these predominantly non-transparent systems.

(1) Light scattering in the samples is one problem. Because there are many phase boundaries with refractive index changes in the samples, it is difficult to calculate the optical path and also the number of absorbed photons per unit volume.

(2) Concentration gradients occur in the samples with adsorbed molecules fixed on particles during the photoreactions. The concentrations of all reacting species are then functions of both time and the position in the

sample. Therefore the direct measurement of such concentration profiles is difficult.

(3) In volume chemistry all molecules are considered to be equal and the concentration is measured in units of moles per volume. Different states exist on the surface and molecules in different states react in different ways. This means that it is not easy to evaluate the real surface concentration for a photoreaction. If diffusion processes occur their influence on the concentration profiles must be taken into account. Only in cases with equilibrium on the adsorbate side can the influence of diffusion be neglected during the (usually) short time of the photoreaction. Any diffusion processes on the surfaces of the separated particles are of no significance if the particle diameters are very small in relation to the depth of penetration of light.

## 2. Experimental technique

One experimental method which has been used to overcome the difficulties outlined in Section 1 is to reduce scattering to a negligible value. This is possible with the immersion technique [6]. Nicholls and Leermakers [2] have investigated photoreactions of adsorbed molecules by this method using weak dehydrated silica gel immersed in cyclohexane or benzene. In this work hydrated silica gel for chromatography (Merck) and cyclohexane were used. Because the optimized transparency is very good (Fig. 1), scattering can be neglected. The preparation of the samples differed in some details from the method described previously. It was important to choose silica gel with only a small range of particle diameters. After the preparation procedure (adsorption from solution and centrifugation) the samples showed no concentration gradient. The concentration profiles were obtained by illuminating the samples in rectangular cells.

To make the theoretical calculations easier we tried to find conditions without concentration profiles. This is the case for two illumination times $t$, i.e. for $t = 0$ (extrapolation to the beginning of the photoreaction, the initial slope method) and for the photostationary state with $t \to \infty$ (this is possible for stable photoproducts in finite times).

It is possible to use relative concentrations if the quantum yields are not functions of concentration. This applies to all monomolecular photoreactions and to bimolecular photoreactions for which the concentration of one species can be kept constant.

For quantitative measurements of the quantum yields of adsorbed molecules we used azines on silica gel [7]. It has been shown [8] that these azines undergo a reversible $E-Z$ isomerization in solution. The same reaction also takes place on hydrated silica gel surfaces. We found that 1-(9-anthryl)-4,4-diphenyl-2,3-diazabutadiene (benzophenone anthracenealdazine, BAA) was especially suitable for our investigations, because the photoreaction is of the type shown in Fig. 2.

The pure $E$ isomer was adsorbed onto silica gel in a rectangular cell. It was irradiated with a known intensity of light (in units of photons cm$^{-2}$ s$^{-1}$) and the optical density was measured as a function of time.
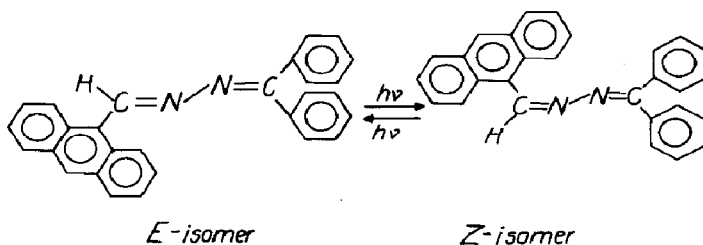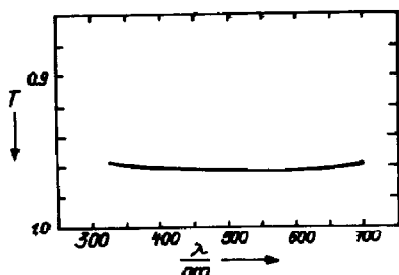
Fig. 1. The transparency of the cyclohexane—silica gel suspension (thickness 1 mm).

Fig. 2. The photoreaction for BAA.

## 3. Kinetics

The following equations are valid for the systems described in Section 2 [9]:

$$-\frac{\partial c_E}{\partial t} = (\varphi_E \epsilon_E c_E - \varphi_Z \epsilon_Z c_Z)I(x)$$

$$\frac{\partial c_Z}{\partial t} = -\frac{\partial c_E}{\partial t} \tag{1}$$

$$\frac{\partial I}{\partial x} = -(\epsilon_E c_E + \epsilon_Z c_Z)I(x)$$

where $I(x)$ is the light intensity at position $x$ in the sample, $\varphi_E$ and $\varphi_Z$ are quantum yields, $\epsilon_E$ and $\epsilon_Z$ are extinction coefficients and $c_E$ and $c_Z$ are concentrations of the $E$ and $Z$ isomers respectively.

Using $\alpha = c_E/c_{E,0}$ and $c_{E,0} = c_E + c_Z$, where $c_{E,0}$ indicates the concentration of isomer $E$ at $t = 0$, we obtain

$$-\frac{\partial \alpha(x,t)}{\partial t} = \{(\varphi_E \epsilon_E + \varphi_Z \epsilon_Z)\alpha - \varphi_Z \epsilon_Z\}I(x,t)$$

and  (2)

$$\frac{\partial I(x,t)}{\partial x} = -\{(\epsilon_E - \epsilon_Z)\alpha + \epsilon_Z\}c_{E,0}I(x,t)$$

As well as these equations the functions $\alpha(x,t)$ and $I(x,t)$ must fulfil the following boundary conditions:

$(\alpha)_{t=0} = 1$     for $0 \leqslant x \leqslant L$       ($L$ is the cell length)

$(I)_{x=0} = I_0$     for $0 \leqslant t < \infty$

At the beginning of the photoreaction, *i.e.* for small $t$, the concentration $c_Z$ is very low so that the back reaction $Z \to E$ is negligible and we find from eqn. (2) that

$$-\left(\frac{\partial \alpha}{\partial t}\right)_{\alpha \approx 1} \approx \varphi_E \epsilon_E \alpha I_0 \exp\left(-\epsilon_E c_{E,0} x\right) \tag{3}$$

Integration of eqn. (3) with respect to $x$ and $t$ then yields

$$\ln\left\{\frac{\exp\left(L\epsilon_E c_{E,0}\right) - 1}{\exp\left(L\epsilon_E c_{E,0}\alpha\right) - 1}\right\} = I_0 \varphi_E \epsilon_E t \tag{4}$$

Equation (4) is identical with that obtained for stirred solutions [9, 10].

To evaluate the quantum yields $\varphi_E$ and $\varphi_Z$ from the kinetic equations, eqns. (2), it is necessary to find two independent relations between these quantities and the optical density $D(L,t)$ of the sample:

$$D(L,t) = -\log\left\{\frac{I(L,t)}{I(0,t)}\right\}$$

$$= \log_e \int_0^L dx \left\{\epsilon_E c_E(x,t) + \epsilon_Z c_Z(x,t)\right\}$$

If the photostationary state is within reach we obtain these relations from the slope of the curve $D(L,t)$ versus $t$ at $t = 0$:

$$\left(\frac{\partial D}{\partial t}\right)_{t=0} = \log_e I_0 \left\{1 - \exp\left(-L\epsilon_E c_{E,0}\right)\right\}(\epsilon_Z - \epsilon_E)\varphi_E \tag{5a}$$

and from the value of $D(L,t)$ in the photostationary state:

$$\lim_{t \to \infty} D(L,t) = \log_e L \left\{(\epsilon_E - \epsilon_Z)\alpha_\infty + \epsilon_Z\right\}c_{E,0} \tag{5b}$$

where $\alpha_\infty$ is given by

$$\alpha_\infty = \frac{\varphi_Z \epsilon_Z}{\varphi_E \epsilon_E + \varphi_Z \epsilon_Z} \tag{5c}$$

which follows from eqn. (2) with $\partial\alpha/\partial t = 0$. Then, using eqns. 5(a) - 5(c), we can determine the quantum yields $\varphi_E$ and $\varphi_Z$ of the photoreaction shown in Fig. 2.

If it is impossible to reach the photostationary state only $\varphi_E$ can be obtained using this method. In this case $\varphi_Z$ can be determined by fitting, with variation of $\varphi_Z$, calculated curves to measured curves of $D(L,t)$ versus $t$.

## 4. Experimental results and discussion

UV–visible spectra of the $E$ isomer, the $Z$ isomer and a mixture of both after illumination are given in Fig. 3. For the photoreaction shown in Fig. 2 we found the values $\varphi_E = 0.031$ and $\varphi_Z = 0.17$ from more than 15 measurements. The quantum yield $\varphi_E$ is a factor of 3 - 10 greater than values obtained from solutions, including solvents of polarity similar to that of silica gel. This indicates a specific influence of adsorption on the photophysical and photochemical processes of this azine [7, 8].
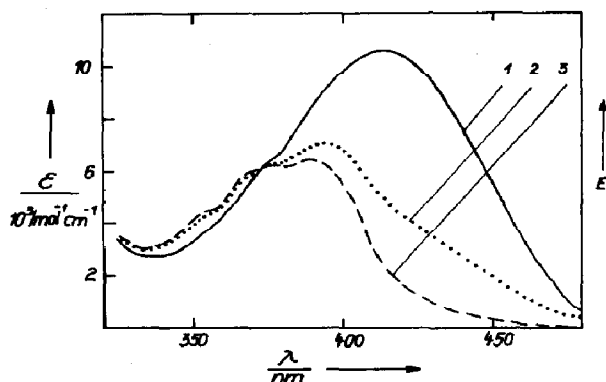
Fig. 3. Absorption spectra of BAA under illumination with light of wavelength 436 nm: curve 1, $E$ iosmer; curve 2, photostationary state; curve 3, $Z$ isomer.

For experimental confirmation of this method we integrated eqns. (2) numerically with values assigned to $\varphi_E$ and $\varphi_Z$. The theoretical and experimental curves obtained are shown in Fig. 4. The local relative concentrations were averaged through the sample thickness and are related to the experimental results by the optical density measurements. The agreement is good and the assumptions used in evaluating the quantum yields seem to be valid.

It was also possible to gain an estimation of the validity of eqn. (3), *i.e.* for neglecting the back reaction $Z \rightarrow E$ (Fig. 5). The agreement is surprisingly good for amounts of the photoproduct $Z$ of less than 20% of the amount of the $E$ isomer. This wide range is associated with the large value of $\epsilon_E/\epsilon_Z$ (of the order of 10), which has greater influence on the whole reaction than the differences in $\varphi$.

The largest errors in $\varphi$ for this method are of the order of 30 - 40%, *i.e.* about the same as those obtained for most photoreactions in solution.
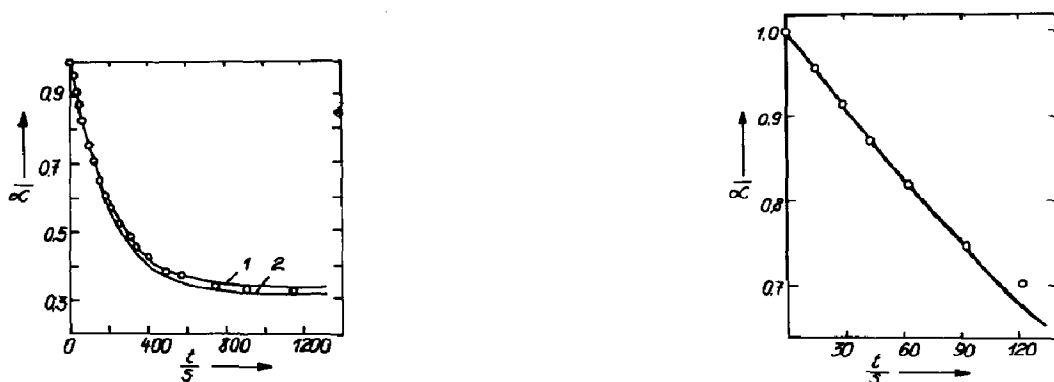




Fig. 4. Concentration–time curves for the photoisomerization of BAA on silica gel: ○, experimental values; ——, values obtained by numerical integration of eqn. (2); curve 1, calculated using $\varphi_E = 0.03$ and $\varphi_Z = 0.172$; curve 2, calculated using $\varphi_E = 0.031$ and $\varphi_Z = 0.163$.

Fig. 5. A concentration–time curve of the photoisomerization of BAA on silica gel; ○, experimental values; ——, calculated using eqn. (4) and $\varphi_E = 0.03$.

This method for evaluating quantum yields of adsorbed molecules can be used if the transparency of the system is sufficiently high. The limitations of the method are the following.

(1) The refractive index of the adsorbent should not have a noticeable anisotropy.

(2) The immersion liquid should have a refractive index value which is quite close to that of the solid adsorbent, so that in most cases we are limited to refractive indices which are less than 1.6.

(3) Because relative concentrations are used, the quantum yield should not be a function of concentration. This is the case for monomolecular reactions, but only occurs for bimolecular reactions when there is a constant concentration (a large excess) of one species during photoreaction.

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