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Journal of Photochemistry and Photobiology A: Chemistry 107 (1997) 27-34

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY

# Determination of quantum yields and product spectra by studying reversible photoisomerizations in solution

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Received 4 July 1996; accepted 25 November 1996

## Abstract

A procedure is presented which combines the method of Fischer (J. Phys. Chem. 71 (1967) 3704–3706) with techniques for calculating the absorbance in the photostationary state, in particular the method of formal integration and that of "transformed time". The proposed procedure thus enables the quantum yields of a reversible photoisomerization as well as the absorption spectrum of the photoproduct to be calculated from a set of reaction spectra $A(t,\lambda)$ measured at sufficiently low exposure times $t$. Finally, using the method presented here, the photoisomerizations of several model compounds were analysed to demonstrate its applicability and performance.

*Keywords:* Product spectra; Quantum yields; Reversible photoisomerizations

## 1. Introduction

Any kinetic analysis of a photochemical reaction requires a knowledge of the absorption coefficients of all the species involved. Although the determination of the absorption coefficients of the reactants is generally not difficult, the evaluation of those of the products often demands considerable effort. This is particularly the case when the photoproduct cannot be prepared in a pure state, e.g. because of poor separability from the reactants or a lack of thermal stability. In this case, the absorption coefficients of the photoproducts may only be determined together with the quantum yields, i.e. by evaluating the rate equations.

The computer program FACSIMILE, frequently used for chemical process assessment and for solving rate equations of complex chemical reactions including diffusion, advective mechanisms and photoinduced gas-phase reactions [1], was not originally planned to describe photochemical reactions in condensed media, such as solutions, and therefore did not seem to be suitable for our purposes.

A simple, but widely used, technique for calculating the quantum yield of photoproduct formation is the "initial slope method" [2]. However, it works only if the absorption coefficients of the product at the irradiation and observation wavelengths are known from direct measurements or if there is at least one wavelength $\lambda_o$ at which the product does not absorb, i.e. $\epsilon_B(\lambda_o) = 0$. In the latter case, in addition to the quantum yield, the absorption coefficient of the product at the irradiation wavelength $\lambda_i$ may be determined.

On the other hand, for reversible photoisomerizations $A \rightleftharpoons B$, Fischer [3] has proposed a method which enables the absorption coefficients of product B to be calculated from the absorbances of the irradiated solution in two different photoequilibrated states. In contrast with the former method, the latter does not require any assumptions concerning the absorption spectrum of the photoproduct. However, its practical application is limited by the fact that, because of side reactions, the photostationary state cannot be attained for a large number of photoreactions.

In this paper, a procedure is presented which combines Fischer's method [3] with two different ways of calculating the absorbance in the photostationary state, i.e.

1. the method of "formal integration" [2,4];
2. the method of "transformed time" [5,6].

By application of this procedure to the kinetic analysis of a number of photoisomerizations, it has been shown that both the absorption spectrum of the product and the quantum

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1010-6030/97/$17.00
*PII* S1010-6030(96)04594-7

yields can be determined for reactions in which the photostationary state cannot be attained.

## 2. Theory

### *2.1. Equations relating the absorption coefficients and the quantum yields to the photostationary state*

The kinetics of reversible photoisomerization

$$A \overset{h\nu}{\rightleftharpoons} B$$

proceeding in a stirred solution, can usually be described by the rate equations

$$\frac{dc_{A\lambda_i}(t)}{dt} = F_{\lambda_i}[\Phi_A^B \epsilon_B(\lambda_i) c_{B\lambda_i} - \Phi_B^A \epsilon_A(\lambda_i) c_{A\lambda_i}] \tag{1}$$

$$\frac{dc_{B\lambda_i}(t)}{dt} = F_{\lambda_i}[\Phi_B^A \epsilon_A(\lambda_i) c_{A\lambda_i} - \Phi_A^B \epsilon_B(\lambda_i) c_{B\lambda_i}] = -\frac{dc_{A\lambda_i}(t)}{dt} \tag{2}$$

where $\lambda_i$ indicates the wavelength of light irradiation and $F_{\lambda_i}$ denotes the so-called photokinetic factor

$$F_{\lambda_i}(t) = I_{\lambda_i}\frac{1-10^{-A_{\lambda_i}(t,\lambda_i)}}{A_{\lambda_i}(t,\lambda_i)} \tag{3}$$

Here $A_{\lambda_i}(t,\lambda_i)$ designates the absorbance of the solution at the irradiation wavelength $\lambda_i$ and $I_{\lambda_i}$ is the intensity of the incident light. Furthermore, $\epsilon_A(\lambda_i)$ and $\epsilon_B(\lambda_i)$ denote the molar absorption coefficients of A and B respectively measured at the wavelength $\lambda_i$, $\Phi_B^A$ designates the partial quantum yield for the formation of B when A is excited and $\Phi_A^B$ designates the partial quantum yield for the reverse case. Provided that the above reaction scheme and hence the rate equations (Eqs. (1) and (2)) are valid for any wavelength $\lambda_i$ from the long-wavelength absorption band of the reactant, the quantum yields $\Phi_B^A$ and $\Phi_A^B$ are considered to be constant within this $\lambda$ range.

Because of Eq. (2), the concentrations of A and B satisfy the balance equation

$$c_{A\lambda_i}(t) + c_{B\lambda_i}(t) = c_0 \tag{4}$$

with the help of which one concentration may be eliminated, so that the remaining rate equation can be rewritten in terms of the dimensionless extent of conversion

$$\alpha_{\lambda_i}(t) = \frac{c_{B\lambda_i}(t)}{c_0} = 1 - \frac{c_{A\lambda_i}(t)}{c_0} \tag{5}$$

which leads to

$$\frac{d\alpha_{\lambda_i}(t)}{dt} = F_{\lambda_i}[m_{\lambda_i} - p_{\lambda_i}\alpha_{\lambda_i}(t)] \tag{6}$$

where $c_0$ denotes the total concentration and the parameters $m_{\lambda_i}$ and $p_{\lambda_i}$ are given by

$$m_{\lambda_i} = \epsilon_A(\lambda_i)\Phi_B^A \tag{7}$$

$$p_{\lambda_i} = \epsilon_A(\lambda_i)\Phi_B^A + \epsilon_B(\lambda_i)\Phi_A^B \tag{8}$$

In order to relate $m_{\lambda_i}$ and $p_{\lambda_i}$ with an appropriate observable, we consider the photostationary equilibrium where the time derivatives of the concentrations and all concentration-dependent quantities vanish, and hence the following relation holds

$$\left(\frac{d\alpha_{\lambda_i}(t)}{dt}\right)_{t\to\infty} = 0 \tag{9}$$

Setting $(d\alpha_{\lambda_i}/dt)$ equal to zero in Eq. (6), we obtain for the extent of conversion $\alpha_{\lambda_i}(\infty)$ in the photostationary state the expression

$$\alpha_{\lambda_i}(\infty) = \frac{m_{\lambda_i}}{p_{\lambda_i}} = \left[1 + \frac{\epsilon_B(\lambda_i)}{\epsilon_A(\lambda_i)}\left(\frac{\Phi_A^B}{\Phi_B^A}\right)\right]^{-1} \tag{10}$$

Since, according to the remarks at the beginning of this section, the quantum yields $\Phi_B^A$ and $\Phi_A^B$ are assumed to be independent of the wavelength, their ratio $\Phi_A^B/\Phi_B^A$ will also be constant within the spectral range considered [7,8].

The absorbance $A_{\lambda_i}(t,\lambda_o)$ of the irradiated sample measured at the observation wavelength $\lambda_o$ as a function of the irradiation time $t$ is apparently given by

$$A_{\lambda_i}(t,\lambda_o) = d[\epsilon_A(\lambda_o)c_{A\lambda_i} + \epsilon_B(\lambda_o)c_{B\lambda_i}] \tag{11}$$

If Eq. (5) is taken into account, the above relationship becomes

$$A_{\lambda_i}(t,\lambda_o) = A_A(\lambda_o) + (A_B(\lambda_o) - A_A(\lambda_o))\alpha_{\lambda_i}(t) \tag{12}$$

where

$$A_A(\lambda_o) = dc_0\epsilon_A(\lambda_o) \tag{13}$$

and

$$A_B(\lambda_o) = dc_0\epsilon_B(\lambda_o) \tag{14}$$

designate the absorbances of the hypothetically pure samples only containing species A and B respectively with the concentration $c_0$. In the limit of infinitely long exposure times $t$, i.e. in the photostationary equilibrium, the absorbance amounts to

$$\begin{aligned} A_{\lambda_i}(t=\infty,\lambda_o) &= A_{\lambda_i}(\infty,\lambda_o) \\ &= A_A(\lambda_o) + (A_B(\lambda_o) - A_A(\lambda_o))\alpha_{\lambda_i}(\infty) \end{aligned} \tag{15}$$

and the corresponding absorbance difference can be expressed as

$$\begin{aligned} \Delta A_{\lambda_i}(\infty,\lambda_o) &= A_{\lambda_i}(\infty,\lambda_o) - A_{\lambda_i}(0,\lambda_o) \\ &= (A_B(\lambda_o) - A_A(\lambda_o))\alpha_{\lambda_i}(\infty) \end{aligned} \tag{16}$$

where the boundary condition $A_{\lambda_i}(0,\lambda_o) = A_A(\lambda_o)$ has been used.

By measuring the absorbance differences between the photoequilibrium and initial states at the wavelengths $\lambda_i$ and $\lambda_o$ and using Eqs. (10) and (16), the following three equations

$$\alpha_{\lambda_i}(\infty)=\left[1+\frac{A_B(\lambda_i)}{A_A(\lambda_i)}\left(\frac{\Phi_A^B}{\Phi_B^A}\right)\right]^{-1}$$

$$\Delta A_{\lambda_i}(\infty,\lambda_i)=(A_B(\lambda_i)-A_A(\lambda_i))\alpha_{\lambda_i}(\infty)$$

$$\Delta A_{\lambda_i}(\infty,\lambda_o)=(A_B(\lambda_o)-A_A(\lambda_o))\alpha_{\lambda_i}(\infty)$$

are obtained, not allowing the four unknown parameters $A_B(\lambda_i)$, $A_B(\lambda_o)$, $\Phi_A^B/\Phi_B^A$ and $\alpha_{\lambda_i}(\infty)$ to be determined in this way.

However, the problem can be solved if, following the method proposed by Fischer [3], two different photostationary states resulting from irradiations at wavelengths $\lambda_1$ and $\lambda_2$ are involved. By choosing the wavelengths $\lambda_1$ and $\lambda_2$ as observation points, using Eqs. (10) and (16) we can establish a total number of six equations

$$\Delta A_{\lambda_1}(\infty,\lambda_1)=(A_B(\lambda_1)-A_A(\lambda_1))\alpha_{\lambda_1}(\infty) \tag{17a}$$

$$\Delta A_{\lambda_2}(\infty,\lambda_2)=(A_B(\lambda_2)-A_A(\lambda_2))\alpha_{\lambda_2}(\infty) \tag{17b}$$

$$\Delta A_{\lambda_1}(\infty,\lambda_2)=(A_B(\lambda_2)-A_A(\lambda_2))\alpha_{\lambda_1}(\infty) \tag{17c}$$

$$\Delta A_{\lambda_2}(\infty,\lambda_1)=(A_B(\lambda_1)-A_A(\lambda_1))\alpha_{\lambda_2}(\infty) \tag{17d}$$

$$\alpha_{\lambda_1}(\infty)=\left[1+\frac{A_B(\lambda_1)}{A_A(\lambda_1)}\left(\frac{\Phi_A^B}{\Phi_B^A}\right)\right]^{-1} \tag{17e}$$

$$\alpha_{\lambda_2}(\infty)=\left[1+\frac{A_B(\lambda_2)}{A_A(\lambda_2)}\left(\frac{\Phi_A^B}{\Phi_B^A}\right)\right]^{-1} \tag{17f}$$

which are obviously not linearly independent. Dividing Eq. (17a) by Eq. (17d) and Eq. (17b) by Eq. (17c), we have

$$\frac{\Delta A_{\lambda_1}(\infty,\lambda_1)}{\Delta A_{\lambda_2}(\infty,\lambda_1)}=\frac{\alpha_{\lambda_1}(\infty)}{\alpha_{\lambda_2}(\infty)}$$

and

$$\frac{\Delta A_{\lambda_1}(\infty,\lambda_2)}{\Delta A_{\lambda_2}(\infty,\lambda_2)}=\frac{\alpha_{\lambda_1}(\infty)}{\alpha_{\lambda_2}(\infty)}$$

from which finally

$$\left(\frac{\Delta A_{\lambda_1}(\infty,\lambda_1)}{\Delta A_{\lambda_2}(\infty,\lambda_1)}+\frac{\Delta A_{\lambda_1}(\infty,\lambda_2)}{\Delta A_{\lambda_2}(\infty,\lambda_2)}\right)=2\frac{\alpha_{\lambda_1}(\infty)}{\alpha_{\lambda_2}(\infty)}$$

results. Thus, by combining this equation with Eqs. (17a), (17b), (17e) and (17f), we may extract the following five linear independent equations

$$\Delta A_{\lambda_1}(\infty,\lambda_1)=(A_B(\lambda_1)-A_A(\lambda_1))\alpha_{\lambda_1}(\infty) \tag{18}$$

$$\Delta A_{\lambda_2}(\infty,\lambda_2)=(A_B(\lambda_2)-A_A(\lambda_2))\alpha_{\lambda_2}(\infty) \tag{19}$$

$$\alpha_{\lambda_1}(\infty)=r\alpha_{\lambda_2}(\infty) \tag{20}$$

$$\alpha_{\lambda_1}(\infty)=\left[1+\frac{A_B(\lambda_1)}{A_A(\lambda_1)}\left(\frac{\Phi_A^B}{\Phi_B^A}\right)\right]^{-1} \tag{21}$$

$$\alpha_{\lambda_2}(\infty)=\left[1+\frac{A_B(\lambda_2)}{A_A(\lambda_2)}\left(\frac{\Phi_A^B}{\Phi_B^A}\right)\right]^{-1} \tag{22}$$

where

$$r=\frac{1}{2}\left[\frac{\Delta A_{\lambda_1}(\infty,\lambda_1)}{\Delta A_{\lambda_2}(\infty,\lambda_1)}+\frac{\Delta A_{\lambda_1}(\infty,\lambda_2)}{\Delta A_{\lambda_2}(\infty,\lambda_2)}\right] \tag{23}$$

Solving Eqs. (18)–(22) for the variables $\alpha_{\lambda_1}(\infty)$, $\alpha_{\lambda_2}(\infty)$, $A_B(\lambda_1)$, $A_B(\lambda_2)$ and $\Phi_A^B/\Phi_B^A$ by a substitution technique finally yields

$$\alpha_{\lambda_1}(\infty)=r\alpha_{\lambda_2}(\infty) \tag{24}$$

$$\alpha_{\lambda_2}(\infty)=\frac{(A_A(\lambda_1)\Delta A_{\lambda_2}(\infty,\lambda_2)-A_A(\lambda_2)\Delta A_{\lambda_1}(\infty,\lambda_1))}{rA_A(\lambda_1)(\Delta A_{\lambda_2}(\infty,\lambda_2)+A_A(\lambda_2))-A_A(\lambda_2)(\Delta A_{\lambda_1}(\infty,\lambda_1)+A_A(\lambda_1))} \tag{25}$$

$$A_B(\lambda_1)=\frac{(A_A(\lambda_1)+\Delta A_{\lambda_1}(\infty,\lambda_1))[rA_A(\lambda_1)\Delta A_{\lambda_2}(\infty,\lambda_2)]}{r(A_A(\lambda_1)\Delta A_{\lambda_2}(\infty,\lambda_2)-A_A(\lambda_2)\Delta A_{\lambda_1}(\infty,\lambda_1))} \tag{26}$$

$$A_B(\lambda_2)=\frac{(A_A(\lambda_2)+\Delta A_{\lambda_2}(\infty,\lambda_2))[rA_A(\lambda_1)\Delta A_{\lambda_2}(\infty,\lambda_2)]}{(A_A(\lambda_1)\Delta A_{\lambda_2}(\infty,\lambda_2)-A_A(\lambda_2)\Delta A_{\lambda_1}(\infty,\lambda_1))} \tag{27}$$

$$\frac{\Phi_A^B}{\Phi_B^A}=\frac{A_A(\lambda_1)A_A(\lambda_2)(r-1)}{rA_A(\lambda_1)\Delta A_{\lambda_2}(\infty,\lambda_2)-A_A(\lambda_2)\Delta A_{\lambda_1}(\infty,\lambda_1)} \tag{28}$$

The above equations show that the ratio $\Phi_A^B/\Phi_B^A$ of the quantum yields, as well as the absorption coefficients $\epsilon_B(\lambda_1)$ and $\epsilon_B(\lambda_2)$ of the photoproduct, are completely determined by the absorption spectrum of the sample in the initial state and the two photoequilibria considered.

### 2.2. *Calculation of the absorbance in the photoequilibrated state*

As noted in the preceding section, the calculation of the quantum yields and absorption coefficients of the photoproducts according to Eqs. (26)–(28) demands a knowledge of the absorption spectrum of the sample in the steady state limit. Unfortunately, the photostationary state of many photoisomerizations is not attainable because, with increasing concentration of the photoproduct, side reactions become more and more important. In such cases, the desired absorbance values $A_{\lambda_i}(\infty,\lambda_o)$ are not available, and have to be calculated from spectroscopic data measured at sufficiently small exposure times such that the influence of side reactions may be neglected.

To calculate the absorbance values required, both the method of formal integration and the method of transformed time are used. The starting point for each of these procedures is a differential equation describing the time dependence of the absorbance $A_{\lambda_i}(t,\lambda_o)$. After differentiating Eq. (13) with respect to time and taking into account Eq. (6), we arrive at

$$\frac{\mathrm{d}A_{\lambda_i}(t,\lambda_o)}{\mathrm{d}t}=F_{\lambda_i}(t)[q_{\lambda_i}(\lambda_o)-p_{\lambda_i}A_{\lambda_i}(t,\lambda_o)] \tag{29}$$

where $q_{\lambda_i}(\lambda_o)$ denotes the expression

$$\begin{aligned} q_{\lambda_i}(\lambda_o) &= m_{\lambda_i} A_B(\lambda_o) + (p_{\lambda_i} - m_{\lambda_i}) A_A(\lambda_o) \\ &= \epsilon_A(\lambda_i)\Phi_B^A A_B(\lambda_o) + \epsilon_B(\lambda_i)\Phi_A^B A_A(\lambda_o) \end{aligned} \tag{30}$$

and $p_{\lambda_i}$ is given by Eq. (8). Time integration of both sides of Eq. (29) from 0 to $t_n$ then yields the formal solution of Eq. (29)

$$A_{\lambda_i}(t_n,\lambda_o) - A_{\lambda_i}(0,\lambda_o) = q_{\lambda_i}(\lambda_o)\int_0^{t_n} dt\, F_{\lambda_i}(t) - p_{\lambda_i}\int_0^{t_n} dt\, F_{\lambda_i}(t) A_{\lambda_i}(t,\lambda_o); \qquad n = 1,\ldots,N \tag{31}$$

an integral equation equivalent to Eq. (29); however, performing the time integration in the opposite direction, i.e. from $t_N$ to $t_n$, leads to the integral equation

$$A_{\lambda_i}(t_n,\lambda_o) - A_{\lambda_i}(t_N,\lambda_o) = q_{\lambda_i}(\lambda_o)\int_{t_N}^{t_n} dt\, F_{\lambda_i}(t) - p_{\lambda_i}\int_{t_N}^{t_n} dt\, F_{\lambda_i}(t) A_{\lambda_i}(t,\lambda_o); \qquad n = N-1,\ldots,0 \tag{32}$$

which has an analogous form to Eq. (31), but is not identical. Compared with the differential Eq. (29), the integral Eq. (31) has the advantage that the integrals

$$\int_0^{t_n} dt\, F_{\lambda_i}(t) = I_{\lambda_i}\int_0^{t_n} dt\, \frac{1 - 10^{-A_{\lambda_i}(t,\lambda_i)}}{A_{\lambda_i}(t,\lambda_i)} \tag{33}$$

and

$$\int_0^{t_n} dt\, F_{\lambda_i}(t) A_{\lambda_i}(t,\lambda_o) = I_{\lambda_i}\int_0^{t_n} dt\, \frac{1 - 10^{-A_{\lambda_i}(t,\lambda_i)}}{A_{\lambda_i}(t,\lambda_i)} A_{\lambda_i}(t,\lambda_o) \tag{34}$$

are easily calculated by means of a numerical approximation formula from the measured absorbance–time curves $A_{\lambda_i}(t,\lambda_i)$ and $A_{\lambda_i}(t,\lambda_o)$ respectively. Dividing Eq. (31) by the integral (Eq. (33)), we obtain ($n = 1,\ldots,N$)

$$\underbrace{\frac{\Delta A_{\lambda_i}(t,\lambda_o)(t_n)}{\int_0^{t_n} dt\, F_{\lambda_i}(t)}}_{y_n} = q_{\lambda_i}(\lambda_o) - p_{\lambda_i}\underbrace{\frac{\int_0^{t_n} dt\, F_{\lambda_i}(t) A_{\lambda_i}(t,\lambda_o)}{\int_0^{t_n} dt\, F_{\lambda_i}(t)}}_{x_n} \tag{35}$$

Hence, a plot of the points $(x_n,y_n)$ should give a straight line of slope $-p_{\lambda_i}$ and intercept $q_{\lambda_i}(\lambda_o)$. The coefficients $q_{\lambda_i}(\lambda_o)$ and $p_{\lambda_i}$ and, according to the formula

$$\frac{q_{\lambda_i}(\lambda_o)}{p_{\lambda_i}} = \frac{m_{\lambda_i}}{p_{\lambda_i}} A_B(\lambda_o) + \left(1 - \frac{m_{\lambda_i}}{p_{\lambda_i}}\right) A_A(\lambda_o) = A_{\lambda_i}(\infty,\lambda_o) \tag{36}$$

the absorbance $A_{\lambda_i}(\infty,\lambda_o)$ in the photoequilibrated state can be determined by a least-squares fit of the points $(x_n,y_n)$ to a linear function.

On the other hand, starting from Eq. (32) and proceeding in a similar manner, we obtain linear relations of the form ($n = 0,\ldots,N-1$)

$$\underbrace{\frac{A_{\lambda_i}(t_n,\lambda_o) - A_{\lambda_i}(t_N,\lambda_o)}{\int_{t_N}^{t_n} dt\, F(t)}}_{y'_n} = q_{\lambda_i}(\lambda_o) - p_{\lambda_i}\underbrace{\frac{\int_{t_N}^{t_n} dt\, F(t) A_{\lambda_i}(t,\lambda_o)}{\int_{t_N}^{t_n} dt\, F(t)}}_{x'_n} \tag{37}$$

Fig. 1 shows that, in cases in which side reactions may be neglected, the points $(x',y')$ from the backward integration define a straight line which coincides with that defined by the points resulting from the forward integration. However, since the former are placed nearer to the origin, the coefficients $p_{\lambda_i}$ and $q_{\lambda_i}(\lambda_o)$ will be computed considerably more accurately if the points of both the forward and backward integrations are taken into account.

The second method to calculate $A_{\lambda_i}(\infty,\lambda_o)$ involves the derivation of an analytical expression for the time dependence of the absorbance $A_{\lambda_i}(t,\lambda_o)$. For this purpose, we separate the variables in Eq. (29) and integrate both sides of the resulting equation from 0 to $t_n$ over time. This gives

$$\ln\frac{q_{\lambda_i}(\lambda_o) - p_{\lambda_i}A_{\lambda_i}(t_n,\lambda_o)}{q_{\lambda_i}(\lambda_o) - p_{\lambda_i}A_{\lambda_i}(0,\lambda_o)} = -p_{\lambda_i}I_{\lambda_i}\Theta(t_n) \tag{38}$$

where the integral

$$\Theta(t_n) = \frac{1}{I_{\lambda_i}}\int_0^{t_n} dt\, F_{\lambda_i}(t) = \int_0^{t_n} dt\, \frac{1 - 10^{-A_{\lambda_i}(t,\lambda_i)}}{A_{\lambda_i}(t,\lambda_i)} \tag{39}$$

denotes the so-called transformed time [5] which is easily calculated for each time step $t_n$ by using the experimental $A_{\lambda_i}(t,\lambda_i)$ curves.

Solving Eq. (38) for $A_{\lambda_i}(t_n,\lambda_o)$ and taking into account Eq. (36), we obtain the expression

$$A_{\lambda_i}(t_n,\lambda_o) = A_{\lambda_i}(\infty,\lambda_o) - (A_{\lambda_i}(\infty,\lambda_o) - A_{\lambda_i}(0,\lambda_o))e^{-p_{\lambda_i}I_{\lambda_i}\Theta(t_n)} \tag{40}$$

describing the $\Theta$ dependence of the absorbance $A_{\lambda_i}(\Theta,\lambda_o)$. If the measured absorbances $A_{\lambda_i}(t_n,\lambda_o)$ are plotted against the $\Theta(t_n)$ values, the resulting points obviously define a kinetic

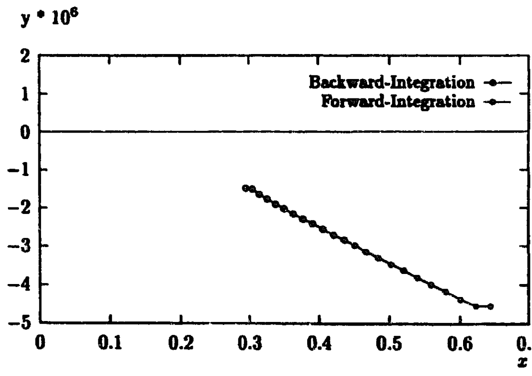

Fig. 1. Plot of the points $(x_n,y_n)$ resulting from "formal integration" for stilbene (ST), $\lambda_i = \lambda_o = 313$ nm.

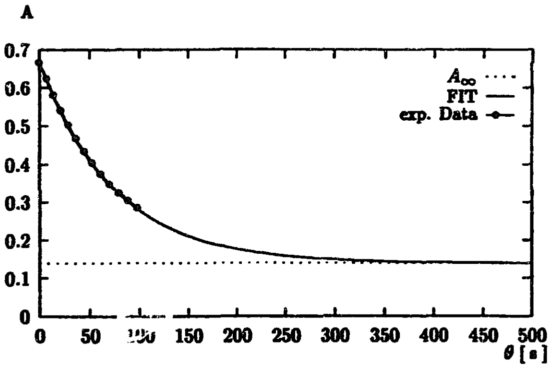

Fig. 2. Illustration of the dependence of $A$ on the "transformed time" $\Theta$ for stilbene (ST), $\lambda_i = \lambda_o = 313$ nm.

curve of the form of Eq. (40) as illustrated in Fig. 2. Thus the desired parameters $A_{\lambda_i}(\infty,\lambda_o)$ and $p_{\lambda_i}$ can be obtained from a least-squares fit of the points $(\Theta(t_n), A_{\lambda_i}(t_n,\lambda_o))$ to an exponential function (Eq. (40)).

## 3. Experimental details

Stilbene (ST) and azobenzene (AZ) were obtained from Merck and were used without further purification. The photoactive substance PNT was obtained from Dr. Haucke and the substance T3 from Professor Grummt (both from the Institute of Physical Chemistry, University of Jena). The compound DMST was synthesized by Dr. Stockmann (Institute of Organic Macromolecular Chemistry, University of Jena). The solvents used for spectroscopic measurements were $n$-hexane and toluene (Merck, UVASOL grade).

The absorption measurements were performed with a SPECORD M400 spectrophotometer (Carl Zeiss, Jena) coupled with an irradiation unit B400 (Carl Zeiss, Jena). The irradiation unit, equipped with an HBO 200 mercury lamp and a high-intensity monochromator, allows monochromatic illumination of the sample to be performed during the absorption measurements. The irradiation intensities needed for the calculations were determined by ferrioxalate [9] and Aberchrome 540 [10] actinometers.

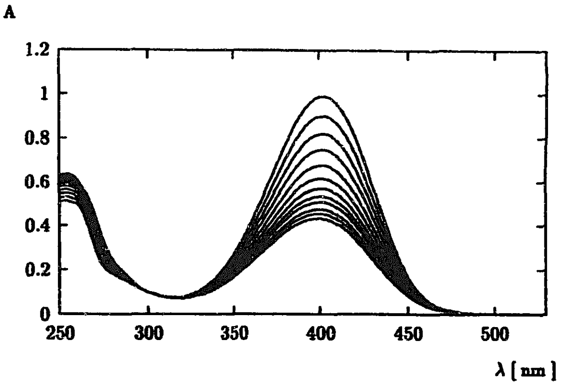

Fig. 3. Spectra of an irradiated solution of compound T3 measured at different exposure times.

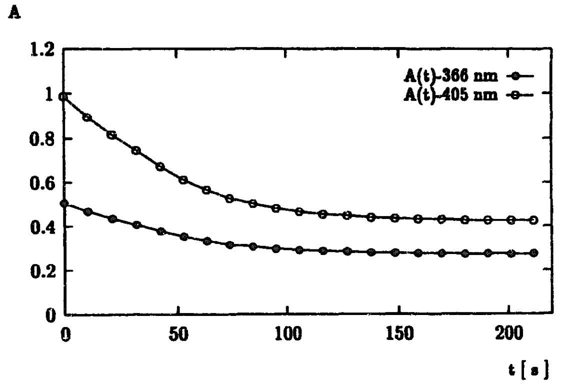

Fig. 4. $A(t)$ curves taken from the reaction spectra at 366 nm and 405 nm.

## 4. Results and discussion

With the help of the method developed in Section 2, the photoisomerizations of the five photochromic compounds listed in Table 1 were studied.

During monochromatic illumination of the corresponding solutions at wavelengths $\lambda_1$ and $\lambda_2$, their absorption spectra were measured for a sequence of exposure times $t_n$ ($n = 0, 1,\ldots,N$). From the two sets of reaction spectra $A_{\lambda_i}(t_n,\lambda_o)$ (i = 1, 2) thus obtained, four absorbance–time curves $A_{\lambda_i}(t_n,\lambda_o)$ were extracted at the observation wavelengths $\lambda_o = \lambda_1, \lambda_2$. In Fig. 3, a set of reaction spectra (T3 illuminated with light of wavelength $\lambda_1 = 366$ nm) is shown and Fig. 4 gives the corresponding absorption–time curves extracted from the spectra at the wavelengths $\lambda_1 = 366$ nm and $\lambda_2 = 405$ nm. From these kinetic curves $A_{\lambda_i}(t_n,\lambda_o)$, using the method

Table 1
List of the compounds studied

| Figure | Solvent | $\lambda_i$ (nm) | Photoactive substance |
|---|---|---|---|
| Fig. 5(a) | $n$-Hexane | 297/313 | Stilbene (ST) |
| Fig. 5(b) | $n$-Hexane | 297/313 | Azobenzene (AZ) |
| Fig. 5(c) | Toluene | 546/577 | 2-(2-Oxonaphtho[1,8-bc]thiopyran-3(2H)-ylidene-naphtho[1,8-bc]thiopyran-3(2H)-one (PNT) |
| Fig. 5(d) | $n$-Hexane | 366/406 | 4-[2-(4-Hydroxyphenyl)ethylene]-1-octadecyl-pyridiniumbromide (T3) |
| Fig. 5(e) | $n$-Hexane | 313/335 | 4,4-Dimethylstilbene (DMST) |

Table 2
Calculated absorption coefficients and quantum yields

| Compound | $\lambda_i$ (nm) | $\lambda^{cal}_{max}$ (nm) | $\lambda^{exp}_{max}$ (nm) | $\epsilon^{cal}_{max}$ (cm$^2$ mmol$^{-1}$) | $\epsilon^{exp}_{max}$ (cm$^2$ mmol$^{-1}$) | $\Phi^B_A$ (calc.) | $\Phi^B_A$ (exp.) | $\Phi^A_B$ (calc.) | $\Phi^A_B$ (exp.) |
|---|---|---|---|---|---|---|---|---|---|
| ST | 313 | 274 | 275 | 10 800 | 11 100 | 0.468 | 0.46 [a] | 0.300 | 0.32 [a] |
| AZ | 313 | 246 | 247 | 13 900 | 12 400 | 0.101 | 0.10 [b] | 0.398 | 0.40 [b] |
| PNT | 577 | 502 | 504 | 17 700 | 17 700 | 0.009 | 0.013 [b] | 0.055 | 0.053 [b] |
| T3 | 366 | 392 | 395 [c] | 6100 | – | 0.283 | – | 0.406 | – |
| DMST | 313 | 281 | 286 [d] | 11 700 | 13 200 [d] | 0.241 | – | 0.266 | – |

[a] See Ref. [3].
[b] See Ref. [11].
[c] See Ref. [12].
[d] See Ref. [13].

of "formal integration" (see Eqs. (35) and (37)) or the method of "transformed time" (see Eq. (40)), the parameters $p_{\lambda_i}$ and $q_{\lambda_i}(\lambda_o)$ and the absorbance values $A_{\lambda_i}(\infty,\lambda_o)$ in the photostationary state were determined. Based on the absorbance values $A_{\lambda_i}(\infty,\lambda_o)$, the product absorbances and the quantum yields were calculated according to Eqs. (24)–(28) and Eqs. (7)–(10).

In contrast with the compounds AZ, PNT and T3, where secondary reactions in general may be neglected, the spectral behaviour of solutions of ST and DMST is strongly influenced by side reactions. To avoid deteriorations of the absorbance values $A_{\lambda_i}(\infty,\lambda_o)$ by side reactions, the photoreactions of ST and DMST were only studied in the conversion ranges $0 \le \alpha_{\lambda_i}(t) < 0.66$ (for ST) and $0 \le \alpha_{\lambda_i}(t) < 0.72$ (for DMST).

In order to obtain the complete product spectrum, the extent of conversion $\alpha_i(t_N)$ was initially determined from the last point of the kinetic curve $A_{\lambda_i}(t_N,\lambda_o)$ using Eq. (13). The reactant absorbance $A_A(\lambda_o)$ also needed here is simply obtained from the spectrum $A_{\lambda_i}(0,\lambda_o)$ of the unirradiated sample. From this spectrum and the last $A_{\lambda_i}(t_N,\lambda_o)$ of the set of spectra considered, by solving Eq. (13) to $A_B(\lambda_o)$, the product absorbance at each point $\lambda_o$ of the spectrum can be calculated easily.

The quantum yields and absorption coefficients of the photoproducts calculated in this way are summarized in Table 2, and Fig. 5(a)–(e) show the calculated product spectra compared with the experimental spectra if available and the spectra of the reactants (i.e. the trans isomers).

As can be seen from Table 2 and Fig. 5(a)–(e), the quantum yields and cis spectra, calculated as described above, are in good agreement with those directly determined from the spectroscopic data of both the trans and cis isomers. However, it should be noted that, in order to obtain reliable quantum yields as well as correct spectra for the cis isomers, the reaction spectra of the irradiated solutions must be measured with high accuracy. If the statistical fluctuations of the absorbance values of the extracted $A(t)$ curve are sufficiently large, the procedure fails in general. In such a case, the parameter $q_{\lambda_i}(\lambda_o)$ will be too small or even negative, so that the absorption coefficients of the photoproduct and the quantum yields are calculated incorrectly. In some cases, even negative values of these quantities are obtained.

Severe errors may also be caused when the first spectra of irradiation series relating to the unirradiated sample differs slightly from each other. The reason for this is that the total concentration $c_0$ is assumed to be the same for irradiations at both wavelengths $\lambda_1$ and $\lambda_2$. If, due to measurement or preparation errors, the spectra of the unirradiated solutions do not coincide, incorrect absorption coefficients of the reactant are determined, which cause deteriorating quantum yields and product absorbances. This deterioration can be avoided by computing an average spectrum from the two different spectra and normalizing the set of reaction spectra with respect to this average spectrum.

Apparently, the spectra of the photoproducts (cis isomers) are independent of the light intensity, whereas the quantum yields are strongly dependent on the light intensity. For this reason, the irradiation wavelengths $\lambda_i$ (i = 1, 2) should be chosen such that the absorption coefficient $\epsilon_A(\lambda_i)$ is sufficiently large, ensuring a high extent of conversion. In addition, the irradiation intensities at these wavelengths must be determined exactly and must only undergo slight fluctuations. On the other hand, the absorption coefficient $\epsilon_B(\lambda_i)$ of the product must not be too low, otherwise the absolute errors in calculating this parameter and the quantum yield of the back reaction will be high. If, at the chosen irradiation wavelength $\lambda_i$, the reactant absorbs much more strongly than the product, the parameter $p_{\lambda_i}$ will be mainly determined by the first term $\epsilon_A(\lambda_i)\Phi^A_B$, whereas the contribution of the second term $\epsilon_B(\lambda_i)\Phi^B_A$ will be negligibly small. In this case, small fluctuations of $p_{\lambda_i}$ cause large errors in $\epsilon_B(\lambda_i)$ and $\Phi^B_A$.

To test both the methods applied to calculate the absorbance in the photoequilibrated state, the product spectra of compound T3 were computed using different numbers of reaction spectra. The results of these computations are shown in Figs. 6–8. From all of these figures, it can be seen that the deterioration of the predicted spectrum of the cis isomer increases with decreasing number of reaction spectra as expected. According to Fig. 6, the simple method of "formal integration" is the most sensitive with regard to the diminution of the number of spectra taken into account. However,

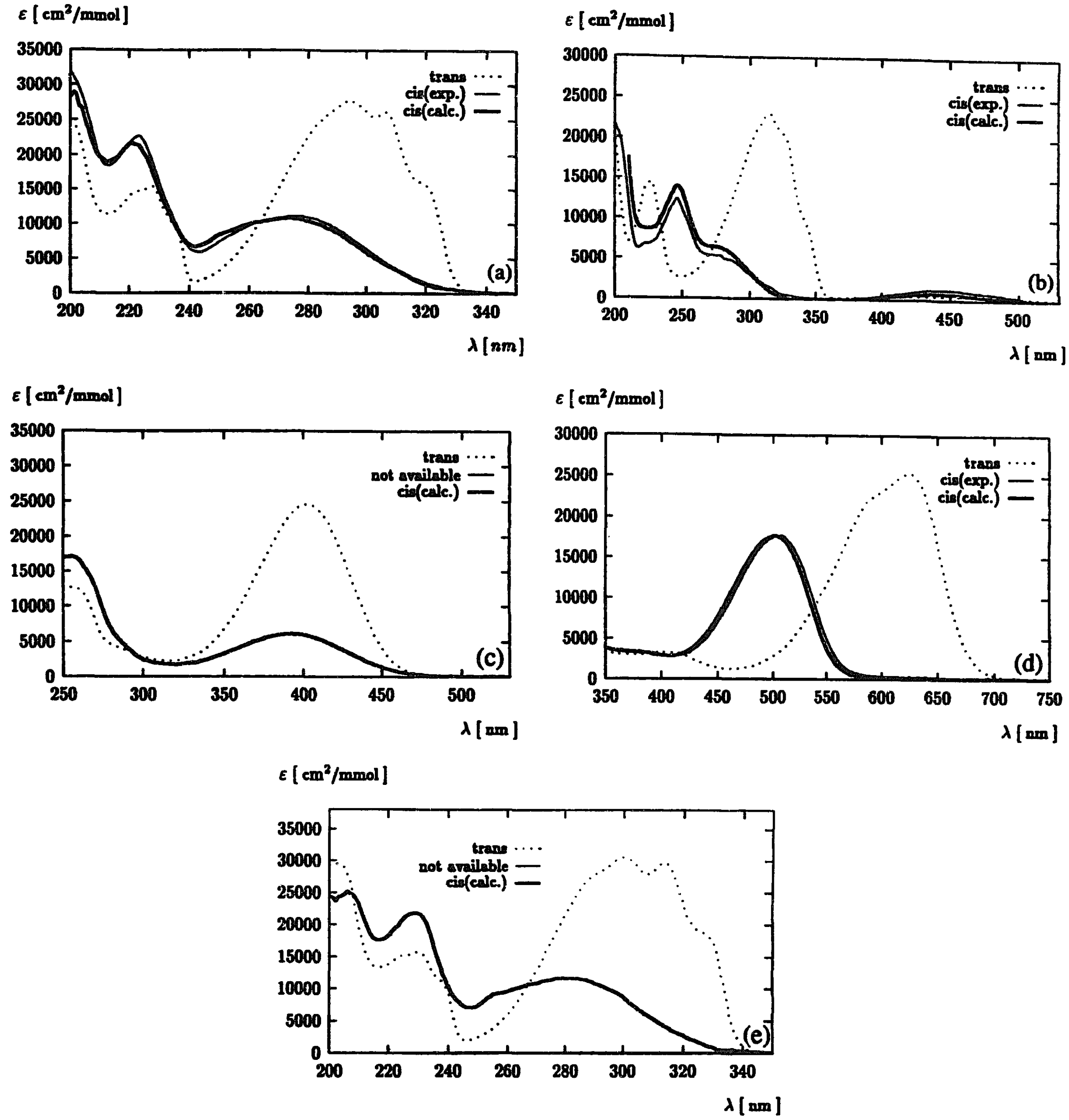

Fig. 5. (a) Calculated and measured spectra of the cis isomer of ST and the spectrum of the trans isomer. (b) Calculated and measured spectra of the cis isomer of AZ and the spectrum of the trans isomer. (c) Calculated and measured spectra of the cis isomer of PNT and the spectrum of the trans isomer. (d) Calculated spectrum of the cis isomer and measured spectrum of the trans isomer of the compound T3. (e) Calculated spectrum of the cis isomer and measured spectrum of the trans isomer of the compound DMST.

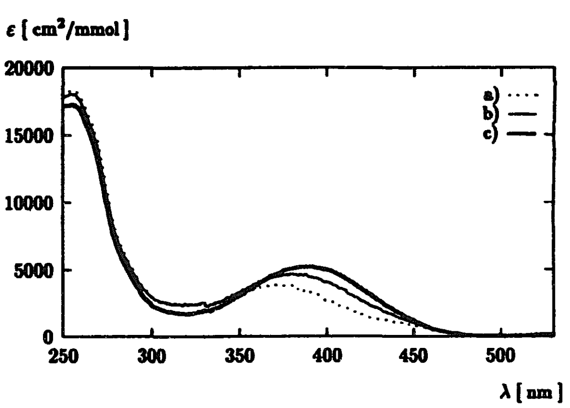

Fig. 6. Results of the simple method of "formal integration" using (a) 9 spectra, (b) 14 spectra and (c) 20 spectra.

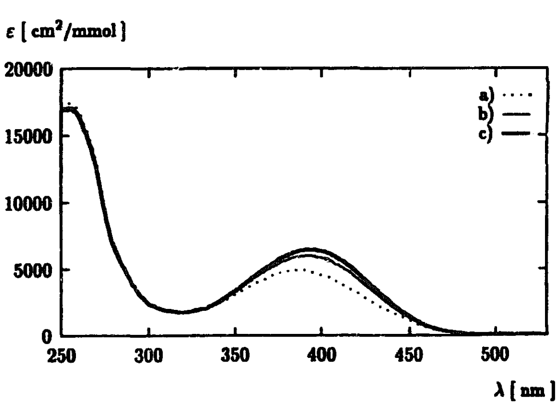

Fig. 7. Dependence of the results of "formal integration", including both forward and backward integration, on the number of spectra used.

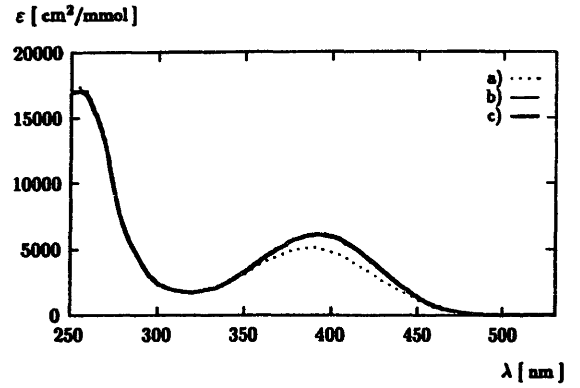

Fig. 8. Influence of the number of spectra used on the results of the method of "transformed time".

Fig. 7 shows that an inclusion of the points resulting from backward integration still leads to a remarkable amelioration of the method. Finally, as illustrated in Fig. 8, the method of "transformed time" is undoubtedly the most accurate and the least sensitive of the methods used to predict the sample absorbances in the photostationary state. This observation conforms to the general experience that the original nonlinear data may usually be fitted more accurately than the linearized data obtained from the former by an appropriate transformation.

## 5. Conclusions

A comparison of the calculated product spectra with those determined directly from isolated cis isomers (Fig. 5(a)–(e)) shows that, for certain experimental conditions, the computed cis spectra agree sufficiently well with the measured "true" spectra. Moreover, as can be seen from Table 2, the partial quantum yields of the photoisomerizations are also calculated quite accurately.

Thus, summarizing, we can state that the method proposed here can calculate both the spectra of the photoproduct and the quantum yields from a set of reaction spectra even if the photostationary state is not attainable experimentally. This method is therefore of particular interest if the photoproduct cannot be isolated by any chemical preparation technique.

## Acknowledgements

We are greatly indebted to our colleagues Dr Haucke, Professor Grummt and Dr Stockmann for supplying us with some of the photoactive compounds studied in this paper.

The research work presented in this paper was financially supported by the Deutsche Forschungsgemeinschaft under contract no. Ga 448/2-2. This support is also gratefully acknowledged.

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