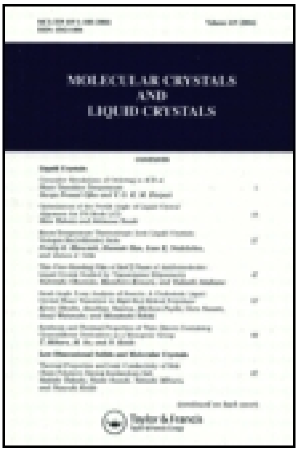

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Photokinetics Under Continuous Irradiation

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PHOTOKINETICS UNDER CONTINUOUS IRRADIATION

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Abstract: This paper show that both direct and reverse quantum yields, the UV/visible spectra of unstable open forms and the quantum yields of photodegradation can be extracted by dynamic modelling and inverse treatment of the plots of Abs *vs* time under continuous irradiation at various selected wavelengths. The basic concepts underlying this dynamic approach are described here using experimental examples in liquid solution. This method was used for a quantitative study of the photochromic spirooxazines. Contrary to fast methods (flash-photolysis), kinetic studies under continuous irradiation are performed under similar conditions to those encountered in natural or industrial environments.

INTRODUCTION

The development of practical applications of photochromic systems requires a source of new compounds and a detailed understanding of the mechanisms involved, including those of the inevitable degradation reactions[1].

Determination of the quantum yields of coloration and bleaching as well as the UV/visible spectra of the colored photoisomers are not readily determined, and generally require a set of observations of the photostationary state. Although theoretically valid, this approach is time consuming, onerous and often lacking in accuracy[2]. Furthermore, it assumes that the reaction mechanism is known and that the system reaches a stable photostationary state, i.e. that there is no photodegradation. To date, there are few reliable experimental measurements of the quantum yields and UV/visible spectra of the unstable photoisomers.

We show here using experimental examples that kinetic modeling and inverse treatment of the plots of Abs *vs* t obtained under monochromatic irradiation of well-stirred photochromic solutions can be employed to extract the characteristic parameters of the photochromic process, namely the quantum yields of photocoloration (ϕ_{AB}) and photobleaching (ϕ_{BA}), and the UV/visible absorption spectrum of the colored photoisomer ($\varepsilon^{\lambda}_{B}$). It can also provide some clues about the macroscopic nature of the reaction mechanism (e.g. origin and estimation of the quantum yield of photodegradation ϕ_{deg},...). Although our method is restricted to photochromic systems with one or more photoisomers of relatively long lifetimes (> 10 s), it is of interest in practical application of photochromism such as variable transmission glasses, which are based on slow systems of this kind. The basic concepts underlying the method will be described briefly below.

CONCEPTUAL FRAMEWORK

Modeling under continuous irradiation is based on an analysis of the plots of Abs *vs* t. It is carried out in a number of stages.

Establishment of the reaction mechanism

Assuming there is no photodegradation, the recognized mechanism is generally schematized as follows:

$$A \rightleftarrows B \qquad (\phi_{AB}, \phi_{BA}, k_{BA}) \qquad \text{(I)}$$

where A is the stable isomer and B the unstable photoisomer linked by two photochemical steps (photocoloration ϕ_{AB} and photobleaching ϕ_{BA}) and by one thermal reisomerization k_{BA} This type of model will be referred to hereafter as « 2ϕ, 1k » since it consists of two photochemical reactions and one thermal reaction. From the equation of conservation of matter:

$$[A_0] = [A] + [B] \qquad (1),$$

a single variable, [A] or [B] or any linear combination, absorbance for example,

$$Abs = \varepsilon_A.[A] + \varepsilon_B.[B] \ (l = 1 \text{ cm}) \qquad (2)$$

is sufficient to describe the kinetic behavior of the system which can be summarized by a single kinetic equation:

$$d[A]/dt = -\phi_{AB}.I_A + \phi_{BA}.I_B + k_{BA}.([A]_0 - [A]) \qquad (3)$$

where I_A and I_B are the volumic photon fluxes absorbed by A and B respectively[3].

Modeling and inverse treatment

In this procedure, the dynamic behavior of the system is modelled and the kinetics are then simulated numerically. In the presence of photochemical processes, the specificity of the photochemical rate law must be taken into account[4]. Thus: $I_A = I_0.\varepsilon'_A.[A].F$ where F is the photokinetic factor[5], which only depends on Abs' (total absorbance); ε'_A is the molar extinction coefficient of A. These two terms have to be taken at the irradiation wavelength λ'. In addition: $I_B = I_0.\varepsilon'_B.[B].F$, and the kinetic equation (3) can be expressed as (4):

$$d[A]/dt = -[(\varphi_{AB} + \varphi_{BA}).F + k_{BA}].[A] + [\varphi_{BA}.F + k_{BA}].[A_0] \qquad (4)$$

characterized by two combined parameters $\varphi_{AB} = \phi_{AB}.\varepsilon'_A.I_0$ and $\varphi_{BA} = \phi_{BA}.\varepsilon'_B.I_0$.
The set of equations (1), (2) and (4) enable numerical calculation of the reaction kinetics and the changes in absorbance.

Inverse treatment is based on a procedure of parameter fitting designed to:

(i) : validate the model: i.e. show that it can accurately describe the experimentally observed plots

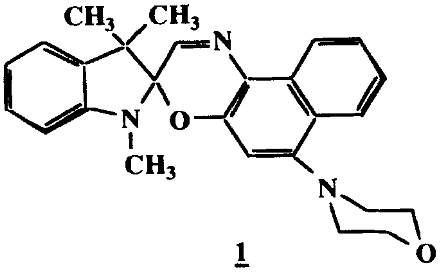
(ii) : extract the characteristic parameters of the photochromic behavior (UV/visible spectrum of B, quantum yields, etc.) .

To analyze a « 2ϕ, 1k » photochemical system, two sets of experiments must be carried out at two different irradiation wavelengths λ' and λ" that are sufficiently close together for $\phi'_{AB} = \phi''_{AB}$ and $\phi'_{BA} = \phi''_{BA}$, but sufficiently distant so that the excitation ratios $\varepsilon'_B/\varepsilon'_A$ and $\varepsilon''_B/\varepsilon''_A$ will be different. The plots of Abs *vs* t are treated simultaneously in an iterative procedure designed to reduce the residual error RE (least squares method) between the curves calculated from the model and the experimentally observed ones. The calculation is initiated by giving each of the parameters an estimated value, which is then optimized over successive iterations such that RE is minimized until the fit of the model to the experimentally observed results is considered acceptable. In this case, the model is validated and optimized parameters are generated. If not, the procedure is carried out again after some adjustment of the model with a modified reaction mechanism.

EXPERIMENTAL RESULTS

1) Photochromism of 5'morpholino-spironaphthoxazine 1

The thermal bleaching is monoexponential ($k_{BA} = 8.10^{-2}\ s^{-1}$ at 278 K).



1

Study of this compound serves to illustrate the principle of the method. Figure 1 shows the simultaneous fitting of the four photochemical kinetics a, b, c and d based on a «2ϕ,1k » model. In this case, there is negligible photodegradation.

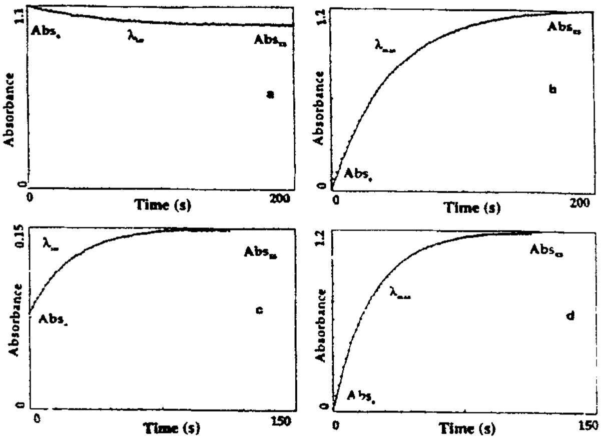


FIGURE 1 Simultaneous fitting of the two photocoloration kinetics
a et b : $[A_0] = 1.10^{-4}$ mol.L^{-1}, $\lambda' = 365$ nm, $\lambda_{obs} = 365$ nm (a) and 570 nm (b)
c et d : $[A_0] = 5.10^{-4}$ mol.L^{-1}, $\lambda' = 405$ nm, $\lambda_{obs} = 405$ nm (c) and 570 nm (d).
$\phi_{AB} = 0.55$; $\phi_{BA} = 0.08$.

The UV/visible spectra of the closed form A (measured) and the open form B (extracted from the inverse treatment) are shown in figure 2.

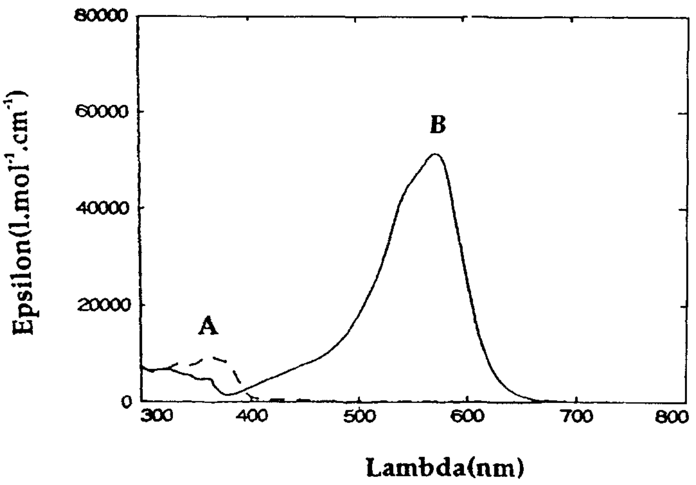


FIGURE 2 UV/visible spectra of closed form (...) and open form (---) of 1.

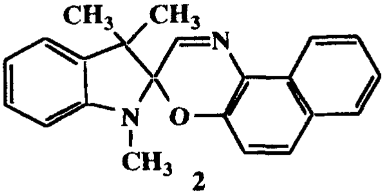
Our results demonstrate the reliability of the method, and indicate that for simple cases akin to this reaction (negligible photodegradation and the presence of a single photoisomer in which recyclization is relatively slow) the photokinetic method gives satisfactory results.

On the other hand, if the mechanism is more complex (photodegradation[6], presence of several photoisomers, as in the case of chromenes), the conservation of matter equation contains more terms (at least one more) and is expressed as:

$$[A_0] = [A] + [B] + [C] \qquad (5)$$

where C represents either a second photoisomer, or the set of photodegradation products. Under these conditions, the kinetics of the reaction cannot be described in terms of a single variable. There is as yet no completely rigorous method for analyzing this type of problem, which may be rather complex in practice. However, in some cases kinetic modeling and inverse treatment may be of value.

2) Photochromism of unsubstituted naphtho-spiro-indolino-oxazine 2



2

Although the irradiation time is relatively brief (t_{irr}< 200 s), the photodegradation reactions have an influence on the photocoloration kinetics. It can be seen by eye that there is a slow decay of the photostationary state on the photocoloration plot at 313 nm, which is indicative of photodegradation.

Our objective was not to study the mechanism of photodegradation in detail, but rather to correct for its possible influence on the photochromic parameters. We assumed that the photodegradation was a single step photochemical reaction from either the closed or open form, each having its own kinetic scheme (Model (a) from the closed form A, or Model (b) from the open form).

Kinetic modeling showed that our results could not be fitted by Model (a). We thus concluded that photodegradation stems from irradiation of the open form B by Model (b).

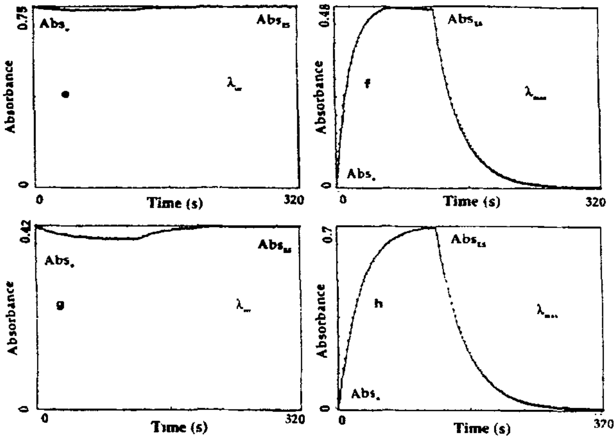


FIGURE 3 Simultaneous fitting of two experiments at two different irradiation wavelengths (313 and 365 nm); photocoloration and thermal bleaching of **2** at 278 K by Model (b). (k_{BA} = 8.10^{-2} s^{-1}) : e et f : λ' = 313 nm ; λ_{obs} = 313 nm (e) et 592 nm (f); g et h: λ' = 365 nm ; λ_{obs} = 365 nm (g) et 592 nm (h). Using Model (b) the same fit is obtained whatever the value of Φ_{BA}, in these conditions the value of Φ_{BC} cannot be extracted. However, the quantum yield of photocoloration, ϕ_{AB} = 0.2, and the UV/visible spectrum of the open form ($\varepsilon'_B \approx 77500$ L.mol^{-1}.cm^{-1}) are relatively independent of the model selected.

Model (a) $C \longleftarrow A \underset{\longleftarrow}{\rightleftarrows} B$

$$d[A]/dt = -\varphi_{AB}.[A].F + \varphi_{BA}.[B].F + k_{BA}.[B] - \varphi_{AC}.[A].F \qquad (6)$$

$$d[B]/dt = - d[A]/dt - \varphi_{AC}.[A].F \qquad (7)$$

Model (b) $A \rightleftarrows B \longrightarrow C$

$$d[A]/dt = -\varphi_{AB}.[A].F + \varphi_{BA}.[B].F + k_{BA}.[B] \quad (8)$$

$$d[B]/dt = - d[A]/dt - \varphi_{BC}.[B].F \quad (9)$$

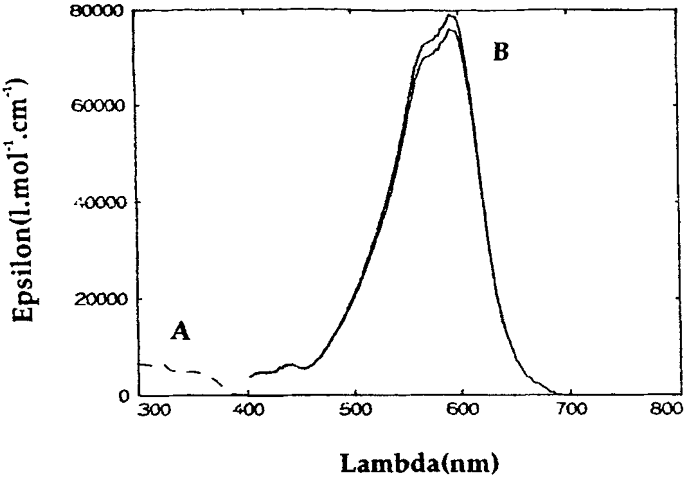


FIGURE 4 UV/visible spectra of spiro-naphtho-oxazine **2** and its open form. Note the slight uncertainty in the determination of ε_B. This was attributed to a too limited experimental information, which did not enable the extraction neither ϕ_{BA} nor ϕ_{BC}.

CONCLUSION

The method of dynamic modeling and inverse treatment was applied to an investigation of the photochromic behavior of two spironaphthooxazines in solution in toluene. The 5'-morpholino derivative **1** is an example of a « 2ϕ,1k » system whose quantum yield values are .55 for the photocoloration (ϕ_{AB}) and .08 for the photodecoloration (ϕ_{BA}). The UV/visible spectrum of the corresponding photomerocyanine was extracted (ε'_B = 52000 L.mol^{-1}.cm^{-1}). For the spironaphthooxazine **2**, the situation was more complex as the experimental observations were unable to provide a value for the quantum yields of photodegradation or photobleaching. However, the quantum yield of photocoloration (ϕ_{AB}) and the UV/visible spectrum of the open form were estimated, and the species undergoing photodegradation (the open form) was identified. These results are in agreement with those reported by other authors (e.g. the quantum yield of photocoloration ϕ_{AB} = 0.2 was comparable to those given by Wilkinson[7] (ϕ_{AB} = 0.23), Kellman[8] (ϕ_{AB} = 0.22) and Favaro[9] (ϕ_{AB} = 0.41 in MCH). On the other hand, there was less agreement with some values found in the litterature about the spectrum of the open form (ε'_B). Our value of $\varepsilon^{612}{}'_B$ = 77500 ±.1500 L.mol^{-1}.cm^{-1}) in toluene may be compared with those of 31000 (Wilkinson[7]), 38000 in MCH (Favaro[10]), 71000 (Chu[11] at low temperature), (73000 (Favaro[9]) and 60000 (estimated by Kelmann *et al.*[8]).

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