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Kinetic Analysis of Photoreversible Photochromic Systems under Continuous Monochromatic Irradiation from Abs. vs Time Curves

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Photoreversible photochromic systems can be analysed quantitatively even if the photoisomers have not been isolated. Quantum yields of photocolouration and photodecolouration and UV / visible spectra of each photoisomer can be extracted simultaneously by numerical simulation and fitting of Abs^t vs time curves recorded under continuous monochromatic irradiation at selected wavelengths.

Keywords: Photochromic parameters – Photokinetic Analysis

I. INTRODUCTION

1,2-diarylethenes¹, fulgides² and azobenzenes³ are of considerable interest for their potential use for practical applications in optical data storage. The absence of back thermal reaction is the main advantage of such photochromic systems.

For the purpose of kinetic modelling, we consider in this paper the so-called (R-1 R-2) system: it is assumed that only two photochemical processes and two photoisomers are involved:



In order to select the most suitable compounds and to establish quantitative structure - properties relationships, an accurate knowledge of all the photochromic parameters is essential: among them are quantum yields Φ_{AB} and Φ_{BA} and UV / visible spectra of both photoisomers. If the two photoisomers have been isolated, the determination is easy. But if only one or none of the photoisomers can be isolated, the problem is more complicated. Two principle techniques are described in the literature, namely those of Fisher⁴ and Wyman⁵. These methods are based on the resolution of photostationary equations and on the assumption that the quantum yields are wavelength independent. They can determine the UV / visible spectra of the photoisomers and their quantum yields ratio Φ_{AB}/Φ_{BA} . Fisher assumes that one photoisomer has been isolated. The calculations show that the problem can be solved

if two steady state UV / visible spectra have been recorded after irradiation at two different wavelengths. Wyman assumes that none of the photoisomers has been isolated. The problem now involves a supplementary unknown (ϵ_A), but Wyman shows that it can be solved by using a third irradiation wavelength. Three steady state UV / visible spectra are needed in this case.

In this paper, we propose a photokinetic analysis of the (R-1 R-2) model. Our method uses Abs vs time kinetic curves recorded under continuous monochromatic irradiation at selected wavelengths. In contrast to the photosteady state methods, the photokinetic analysis of the (R-1 R-2) system produces both quantum yields Φ_{AB} and Φ_{BA} .

II. PHOTOCHEMICAL RATE LAW OF THE (R-1 R-2) SYSTEM

Under monochromatic continuous irradiation⁶ and assuming that the reacting solution is homogeneous, the evolution of the (R-1 R-2) system can be described by a unique differential equation⁷:

$$d[A]/dt = -(\Phi_{AB} \epsilon_A [A] - \Phi_{BA} \epsilon_B [B]) I_0 I_r F' \quad [\text{eq.1}]$$

where F' stands for the photokinetic factor,

$$F' = (1 - 10^{-\text{Abs}'}) / \text{Abs}' \quad [\text{eq.2}]$$

and

$$\text{Abs}' = (\epsilon'_A [A] + \epsilon'_B [B]) l_r \quad [\text{eq.3}]$$

$[A]$ and $[B]$ are linked by the mass balance equation: $[A] + [B] = [M]_0$ [eq.4]

As a consequence, the absorbance is always a linear function of $[A]$. Kinetic systems exhibiting this property are known as monovariab⁸, they are recognisable by the presence of one or more isosbestic points and / or by the linearity of absorbance plots ($\text{Abs}^{\lambda_1}(t)$ vs $\text{Abs}^{\lambda_2}(t)$). The parameters used in this paper are presented in the Table 1.

Symbol or abbreviation	Units	Significance
$[X]$	mol.L ⁻¹	concentration of product X
Φ_{AB}	adimensional	quantum yield of the photochemical reaction $A \rightarrow B$ (h ν)
ϵ'_X ; $\epsilon_X^{\lambda'}$	L.mol ⁻¹ .cm ⁻¹	molar extinction coefficients of product X at irradiation (λ') and monitoring (λ) wavelength;
I_0	mol.L ⁻¹ .s ⁻¹	monochromatic irradiation photon flux at wavelength λ'
l_r	cm	photochemical reactor irradiation optical path
$\text{Abs}^{\lambda'}$	adimensional	Absorbance of the solution at λ

TABLE 1: Significance of symbols and abbreviations.

III. PHOTOKINETIC RUNS AND DATA TREATMENT

1. Simulated data

In order to check if the proposed photokinetic analysis was able to extract the values of the photochromic parameters, several runs have been simulated using [eq. 1 to 4]. They were then submitted to a curve fitting to check if the original values of the photochromic parameters could be retrieved. Such Abs^λ vs time kinetic curves with simulated "experimental" points and continuous fitted lines are shown on figure 1.

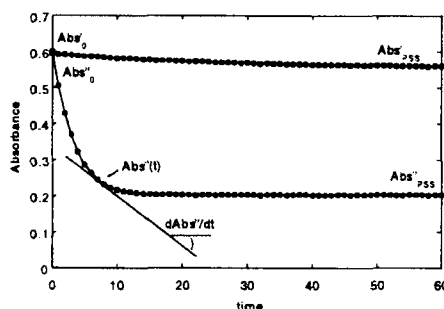


Figure 1: Absorbance vs time photokinetics under continuous monochromatic irradiation at λ' and λ'' of a (R-1,R-2) system with the following values of the photochromic parameters ($\epsilon'_A = 15000$, $\epsilon''_A = 44000$, $\epsilon'_B = 23000$, $\epsilon''_B = 4000$, $\Phi_{AB} = .22$, $\Phi_{BA} = .18$, $I'_0 = 4 \times 10^{-6} \text{ mol.L}^{-1} \cdot \text{s}^{-1}$, $I''_0 = 20 \times 10^{-6} \text{ mol.L}^{-1} \cdot \text{s}^{-1}$, $[A]_0 = 1.2 \times 10^{-5} \text{ mol.L}^{-1}$ and $[M]_0 = 3.0 \times 10^{-5} \text{ mol.L}^{-1}$). Kinetics are shown at the corresponding irradiation wavelength. Dots: simulated "experimental" points with random noise of $\pm .002 \text{ Abs. unit}$ added; continuous lines: numerical fitting.

2. Analysis of the photokinetic data of the (R-1 R-2) photochromic system

For a monovariate system, any experimental kinetics as shown in figure 1 can be described by [eq.5]: $Abs^\lambda(t) = (Abs^\lambda_0 - Abs^\lambda_{PSS})G(t) + Abs^\lambda_{PSS}$ [eq.5] where $G(t)$ is a characteristic time function which is independent on the monitoring wavelength λ and PSS stands for the photosteady state *i.e.* $d[Abs]/dt = 0$. From a single kinetic run monitored at λ' , experimental data are obtained by measuring the initial absorbance (Abs^λ_0), the photosteady state absorbance (Abs^λ_{PSS}), the current absorbance ($Abs^\lambda(t)$) and the photokinetic slope $dAbs^\lambda(t)/dt$. These data are governed by three new relationships ([eq. 6, 7 and 8]) deriving from [eq. 1 to 4]. In [eq. 6, 7 and 8], unknown photochromic parameters (ϵ'_A , ϵ'_B , Φ_{AB} and Φ_{BA}) have been merged on the right side.

a)-: the initial absorbance: $Abs'_0 = (\epsilon'_A - \epsilon'_B)[A]_0 + \epsilon'_B [M]_0$ [eq. 6]

b)-: the photosteady state absorbance:

$$Abs'_{PSS} / [M]_0 = [(\epsilon'_A \epsilon'_B (\Phi_{AB} + \Phi_{BA}) / (\epsilon'_A \Phi_{AB} + \epsilon'_B \Phi_{BA}))] \quad [eq. 7]$$

c)-: the current slope:

$$(dAbs'(t)/dt) / [(Abs'_{PSS} - Abs'(t)) (I_0 F')] = (\epsilon'_A \Phi_{AB} + \epsilon'_B \Phi_{BA}) \quad [eq. 8]$$

Numerical fitting of the experimental data uses the information of the photokinetic curves to extract the values of the unknown photochromic parameters. We will now consider situations that are likely to be encountered experimentally, depending on the number of pure photoisomers that have been isolated (2, 1 or 0). The purpose of this discussion is to see if the information that is obtained from the available photokinetic curves is sufficient to extract all the required unknown parameters.

3. A and B have been isolated

If both photoisomers A and B have been isolated, ϵ^A_A and ϵ^A_B are known as well as Abs'_0 . In these conditions, any photokinetic run provides a sufficient information to determine the two unknown parameters Φ_{AB} and Φ_{BA} using the initial slope in [eq. 9] (deriving from [eq. 8]) and the photosteady state absorption in [eq.10] (from [eq. 7]).

$$\Phi_{AB} = (dAbs'/dt)_0 / [(\epsilon^A_B - \epsilon^A_A) I_0 (1 - 10^{-\epsilon^A_A [A]_0 t_r})] \quad [eq. 9]$$

$$\Phi_{BA} = (\Phi_{AB} \epsilon'_A / \epsilon'_B) (Abs'_{PSS} - \epsilon'_B [A]_0) / (\epsilon'_A [A]_0 - Abs'_{PSS}) \quad [eq. 10]$$

4. Only A has been isolated (Fisher's case)

If A has been isolated, its spectrum (ϵ^A_A) is known, as well as its initial absorption Abs'_0 . In these conditions, a single photokinetic run is not sufficient for the determination of three unknown parameters: ϵ'_B , Φ_{AB} and Φ_{BA} , because there are more unknown parameters than independent relationships. However, the record of a second kinetic run using a second irradiation wavelength (λ'' must be selected so that the epsilon ratio is different ($\epsilon''_B / \epsilon''_A \neq \epsilon'_B / \epsilon'_A$)) provides two more independent relationships and brings only one more unknown (ϵ''_B). The situation is now solvable with 4 independent relationships and 4 unknown parameters.

5. Neither A nor B have been isolated (Wyman's case)

This situation corresponds to the most general case. [eq.6 to 8] provide three independent relationships, but as there are four unknown parameters: ϵ'_A , ϵ'_B , Φ_{AB} and Φ_{BA} , a second irradiation wavelength (λ'') is required in order to provide three more independent relationships. Although two more unknown are added (ϵ''_A and ϵ''_B), the problem is still solvable with 6 unknown parameters and 6 independent relationships. However, in these last two cases, determinations are not feasible by hand calculations and a curve fitting procedure is required.

6. Curve Fitting

Personal computers are now of sufficient power for numerical simulation and fitting for these photokinetic calculations. Changing the experimental conditions (I_0 , $[M]_0$, λ), several experimental photokinetic curves (Abs^k vs t) are recorded. Recording a second monitoring wavelength provides overdetermination which make easier the treatment of noisy data. These experiments are then simulated numerically using [eq. 1 to 4] and roughly estimated values of the unknown parameters. An error function $EF = \sum_p \sum_k (Abs_{exp} - Abs_{sim})^2$ between experimental (Abs_{exp}) and simulated absorbances (Abs_{sim}) is computed, it takes into account n irradiation wavelengths, p monitored wavelengths and k measurement times so that npk experimental points are fitted simultaneously. During this computation, the values are automatically varied until a minimum in EF is obtained. Several starting values of the unknown parameters must be tried in order to check that the calculation is not trapped into a false minimum and that the optimized set is unique. At the end of the calculation, the conversion rate has been determined and quantitative UV / visible spectra of each photoisomer can be calculated from the recorded mixture spectra using [eq.2] and [eq.3]. From the experiment shown on figure 1, quantum yields were extracted within an error of less than $\pm 6\%$ and the molar extinction coefficients with a less than $\pm 4\%$.

IV) CONCLUSION

This paper shows that photokinetic analysis of $Abs.$ vs time curves recorded under continuous monochromatic irradiation of (R-1 R-2) systems provides a more complete information than photostationnary methods. Apart from the absorbance at the steady state, it takes into account the initial absorbance and the current slope. Individual quantum yields rather than just their ratio are obtained. Moreover, even if both photoisomers cannot be isolated, photochromic parameters can be extracted using only two irradiation wavelengths instead of three in the Wyman's method.

The photokinetic method can also be applied when one photoisomer is not stable and undergoes a spontaneous (thermal) return to the starting product or when there is a photodegradation process. Spiropyrans⁹, spirooxazines¹⁰, dihydroindolizines¹¹ azobenzenes¹² and chromenes¹³ are among the most well known thermally bleaching organic photochromes. The conversion rate at the photosteady state depends not only on the irradiation wavelength, but also on the incident photon flux¹⁴ and on the temperature¹⁵. In these case, monovaryable systems are recognized by the presence of a monoexponential thermal decay. In these conditions, they are easy to handle, provided that the thermal decay kinetics has been measured independently and taken into account¹⁶.

Photodegradation is a parasitic phenomenon that is characterised by a slow decay of the photochromic process: a loss of photocolourability and / or the impossibility to obtain a complete bleaching¹⁷. Photodegradation could be significantly slowed down if the reactions that are responsible of the decay were sufficiently understood¹⁸. In the case of thermally bleached photochroms, a photokinetic analysis can to discriminate between a light-promoted or a dark degradation process¹⁹.

References

- [1] a)- M. Irie and M. Mohri *J. Org. Chem.*, **53**, 803 (1988). b)- M. Hanazawa, R. Sumiya, Y. Horikawa, M. Irie. *J. Chem. Soc., Chem. Commun.* 206 (1992).
- [2] a)- J. Whittall, in *Photochromism. Molecules and Systems*, edited by H. Durr and H. Bouas-Laurent (Elsevier. Amsterdam, 1990), Chap. 9.
b)- H.G. Heller, R.J. Hart and K. Salisbury, *J. Chem. Soc., Chem. Commun.*, 1627 (1968).
c)- Y. Yokoyama, T. Yamane, Y. Kurita, *J. Chem. Soc. Chem. Commun.*, 1722 (1991).
- [3] P.H. Rasmussen, *J. Amer. Chem. Soc.* **121** (20), 4738 (1999).
- [4] E. Fisher, *J. Phys. Chem.* **71**, 3704 (1967).
- [5] G. Wyman, *Mol. Photochem.* **6**, 81 (1974).
- [6] M.H. Deniel, D. Lavabre, J.C. Micheau, in *Organic Photochromic and Thermochromic Compounds* (Vol.2) edited by J.C. Crano and R. Guglielmetti (Kluwer Acad. Plenum Press. New York. 1999).
- [7] B. Borderie, D. Lavabre, J.C. Micheau, J.P. Laplante, *J. Phys. Chem.* **96**, 2953 (1992).
- [8] J. Polster and H. Mauser, *J. Photochem. Photobiol. A: Chem.* **43**, 109 (1988).
- [9] V. Pimienta, D. Lavabre, G. Levy, A. Samat, R. Guglielmetti and J.C. Micheau, *J. Phys. Chem.* **100**, 4485 (1996).
- [10] M.H. Deniel, J. Tixier, B. Houzé-Luccioni, D. Lavabre and J.C. Micheau, *Mol. Cryst. Liq. Cryst.*, **298**, 121 (1997).
- [11] M.H. Deniel, J. Tixier, D. Lavabre, J.C. Micheau and H. Dürr *Mol. Cryst. Liq. Cryst.*, **298**, 129 (1997).
- [12] G. Gauglitz, P. Stössel, H. Meier and H. Rau, *J. Photochem. Photobiol. A: Chem.* **85**, 207 (1995).
- [13] B. Van Gemert in *Organic Photochromic and Thermochromic Compounds* (Vol.1) edited by J.C. Crano and R. Guglielmetti (Kluwer Acad. Plenum Press. New York, 1999).
- [14] F. Wilkinson, J. Hobley and M. Naftaly, *J. Chem. Soc. Farad. Trans.* **88**, 1511 (1992).
- [15] G. Favaro, V. Malatesta, U. Mazzucato, G. Ottavi and A. Romani, *J. Photochem. Photobiol. A: Chem.* **87**, 235 (1995).
- [16] R. Bär and G. Gauglitz, *J. Photochem. Photobiol. A: Chem.* **46**, 15 (1989).
- [17] a)V. Malatesta, M. Milosa, R. Millini, L. Lanzani, P. Bortolus and S. Monti, *Mol. Cryst. Liq. Cryst.*, **246**, 303 (1994).
b) V. Malatesta, C. Neri, M.L. Wis, L. Montanari and R. Millini, *J. Amer. Chem. Soc.* **119**, 3451 (1997).
c) V. Malatesta, *Mol. Cryst. Liq. Cryst.*, **298**, 69 (1997).
- [18] C. Salemi-Delvaux, B. Luccioni-Houze, G. Baillet, G. Giusti and R. Guglielmetti, *J. Photochem. Photobiol. A: Chem.* **91**, 223 (1995).
- [19] V. Pimienta, C. Frouté, M.H. Deniel, D. Lavabre, R. Guglielmetti and J.C. Micheau, *J. Photochem. Photobiol. A: Chem.* **122**, 199 (1999).