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KINETIC ANALYSIS OF FLUORO-[2H]-CHROMENES AT THE PHOTOSTATIONARY STATES.

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ABSTRACT : This paper presents the first results obtained in our laboratory, on a U.V-Visible spectrometer at the PhotoStationary State in toluene and ethanol solutions. Here, the multikinetics of fluoro-substituted chromenes are studied with a polychromatic light source in different conditions. The fluoro-substitution on the aryl moiety always leads to an increase of the fast rate constant.

INTRODUCTION :

The Chemistry of spiro compounds has recently become particularly important in connection with the rapid development of optical materials.¹⁻³ It seems now well established that U.V. irradiation of the spiro-form produces several isomeric open-forms.⁴

First investigations on [2H]-chromenes,⁵ were carried out and we have also recently started studies on multikinetics of chromenes in toluene and ethanol solutions.

In this work, we describe kinetic analysis of four chromenes at the PhotoStationary States.

A best knowledge of the photochromic parameters is of great interest to design new active compounds for industrial applications.

EXPERIMENTAL :**Materials :**

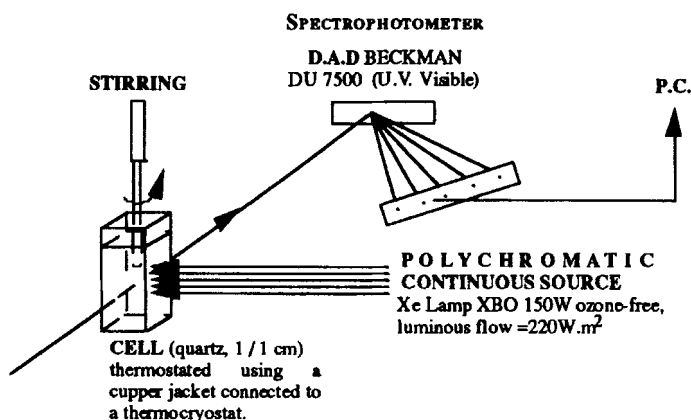
The fluoro-[2H]-chromenes were synthesized according to standard procedures^{6,7} in our laboratory. Solvent were carefully dried and distilled prior to use.

U.V.-Visible detection :

Spectra of photomerocyanine maximum absorption wavelength were obtained in anhydrous toluene (SDS France) or in ethanol (RPE Carlo Erba France) with a system DAD Beckman DU 7500.

Photostationary states experiments :

The photochromic compounds (**1**, **2**, **3**, **4**) ($C = 10^{-4}$ mol.L⁻¹) were dissolved in anhydrous toluene or in ethanol. The irradiation was derived from a Oriel 150 W high-pressure xenon lamp equipped with diaphragm and aqueous solution which removed most of the infrared radiation. Polychromatic light intensity was determined by a Oriel quantum photoradiometer. The quartz analysis cell was enclosed in a thermostated copper block placed inside the sample chamber of a Beckman DU 7500 diode array spectrophotometer. The cell had an optical path length of 1 cm. The aerated solutions were stirred continuously using a mechanical stirrer. This apparatus is described on scheme 1 :



SCHEME 1 : PhotoStationary States Apparatus.

Spectra of photostationary mixtures were obtained in different conditions, at the open form maximum absorption wavelength.

For all compounds, the multikinetics were calculated with PC Grafit 3.0 software, using this equation :

$$f(t) = A_{o1} \cdot \exp(-k_1 \cdot t) + A_{o2} \cdot \exp(-k_2 \cdot t) + \text{off} \quad \text{eq 1}$$

A_{o1} = maximal absorbance at the photostationary state

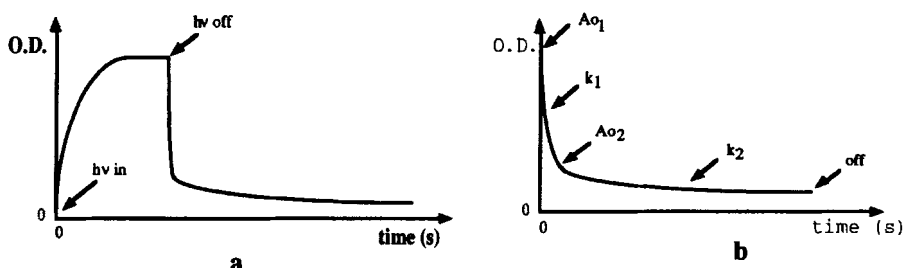
k_1 = first (fast) thermal bleaching rate constant

A_{o2} = maximal absorbance for the second kinetic

k_2 = second (slow) thermal fading rate constant

off = residual absorbance

These previews parameters are drawn up on scheme 2.



SCHEME 2 : a Theoretic spectrum of photostationary mixtures.

b Theoretic bleaching curve of photostationary mixtures.

RESULTS AND DISCUSSION :

Up to now, previous studies⁸⁻¹¹ in our laboratory, gave some informations on kinetic obtained using flash-photolysis. However, this method presents some lacks and does not simulate real conditions of photochromic compounds utilization.

Recently, we start setting up a computer-controlled PhotoStationary States Apparatus designed to analyse bleaching processes using continuous source. Our objective was to mimic the solar irradiation also we used a polychromatic light source. In this method, a second rate constant k_2 can be distinguished and mesured.

Using eq. 1, all the photochromic parameters obtained from 1-4 at the photostationary state in different solvent are extracted and collected in Table 1.

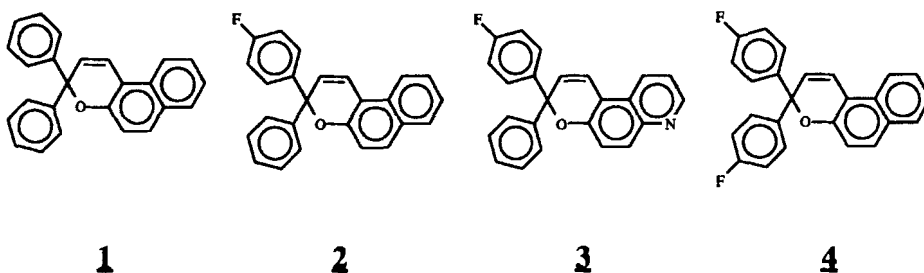
First experiments on spiropyrans¹² have shown that the photomerocyanines (open-forms) were transformed into the starting compounds (closed form) by thermal back-isomerisation or under visible irradiation. Our results confirm that on switching off the irradiation, the thermal or photochemistry biexponential back-isomerization is always observed from **1-4**.

Conceivably, these two different kinetics could be attributed to two different isomers of the open-form.

It is important to note that in all instances, the slow rate constant remains unchanged while the fast rate constant increases with the temperature.

An odd behavior emerges of the compound **3** in the quinoline serie. This compound presents a great solvent dependence.

On the other hand, para-fluoro substitutions on the aryl groups of **4** result in a hypsochromic shift for the colored species.



COMPOUNDS	TOLUENE $C = 10^{-4} \text{ mol.l}^{-1}$			ETHANOL $C = 10^{-4} \text{ mol.l}^{-1}$		
	λ_{obs} (nm)	$k_{\Delta} \cdot 10^3 \text{ (s}^{-1}\text{)}$ T = 283K	$k_{\Delta} \cdot 10^3 \text{ (s}^{-1}\text{)}$ T = 303K	λ_{obs} (nm)	$k_{\Delta} \cdot 10^3 \text{ (s}^{-1}\text{)}$ T = 283K	$k_{\Delta} \cdot 10^3 \text{ (s}^{-1}\text{)}$ T = 303K
1	432	fast : 22.5 slow : 0.1	fast : 163.9 slow : 0.3	434	fast : 20.4 slow : 0.9	fast : 202.8 slow : 0.5
2	448	fast : 61.2 slow : 0.3	fast : 276.4 slow : 0.4	450	fast : 58.0 slow : 0.4	fast : 279.5 slow : 0.5
3	440	fast : 48.7 slow : 0.7	fast : 317.1 slow : 0.3	447	fast : 73.0 slow : 0.7	fast : 973.9 slow : 0.9
4	429	fast : 43.5 slow : 0.2	fast : 683.2 slow : 0.3	431	fast : 37.6 slow : 0.5	fast : 575.7 slow : 0.4

TABLE 1 : Spectrokinetic data at PhotoStationary State.

From these first data obtained at the photostationary states, it emerges that the fluoro-substitution on aryl always leads to an increase of the fast rate constant, however polar the solvent may be.

The quantum yield of the reaction is also an important factor, but not possible to assess without a monochromatic light.

Finally, we shall now extend our investigation to a wider variety of chromenes and under different experimental conditions.

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