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Effect of photodegradation on the thermal bleaching rate constant of photochromic compounds in spiro[indoline-pyran] and spiro[indoline-oxazine] series

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Abstract

The chemistry of spiro compounds has recently become particularly important in association with the rapid development of optical materials. However, photochromic compounds (thermal reversible dyes on light activation) are involved in secondary oxidative photodegradation reactions leading to the loss of their photochromic properties. Variation of the rate constant of thermal ring closure (k_Δ) during photodegradation experiments has been reported in toluene solution for a large number of photochromic molecules (spiro[indoline-naphthoxazine], spiro[indoline-naphthopyran], spiro[indoline-benzopyran] and spiro[indoline-benzoxazine]). Benzoic acid derived from the oxidation of toluene is involved in the process.

Keywords: Photochromic compounds; Photodegradation; Thermal bleaching rate constant; Acceleration; Oxidation; Protonation

1. Introduction

Owing to their ability to undergo photoinduced reversible colouration [1,2], photochromic compounds are very interesting substances for numerous industrial applications (ophthalmic lenses, recording materials). The reversible cleavage of the C–O spiro bond of the colourless form leads to a deeply coloured open form or photomerocyanine, generally in different stereoisomers [3]. The reclosure of the spiro ring is a reverse reaction which can be induced thermally or photochemically (Scheme 1). The rate of thermal reversion of the merocyanine to the spiro compound is controlled by various factors, such as the substitution pattern, temperature and polarity of the medium. Another factor relevant to this kinetic variation is the structure of the open forms generated on light irradiation [4–6]. For example, the addition of an acid may induce a significant change in the rate constant of thermal decolouration of the photochromic compounds, probably by protonation of the open forms.

2. Results and discussion

Since the discovery of the photochromism of indolino spirobenzopyrans by Fischer and Hirshberg [7] in 1952, this family and other related spiropyrans have been studied extensively [1,2]. The most responsive indolino spiropyrans are those bearing a nitro group on the benzopyran moiety of the molecule. Unfortunately, the spiropyrans and, in particular, the nitrospiropyrans have very poor resistance to photochemically induced degradation [8], which represents a major problem that must be solved prior to the industrial utilization of these photochromic systems [9–11]. The partial solution of this problem involves the synthesis of the indolino spironaphthoxazines, a series inherently more resistant to fatigue than the spiropyrans.

Another limiting factor for the industrial application of these photochromic molecules is that the decolouration rate is too slow in a solid matrix. Thus a means to allow the enhancement of this rate constant could be very interesting from an industrial viewpoint.

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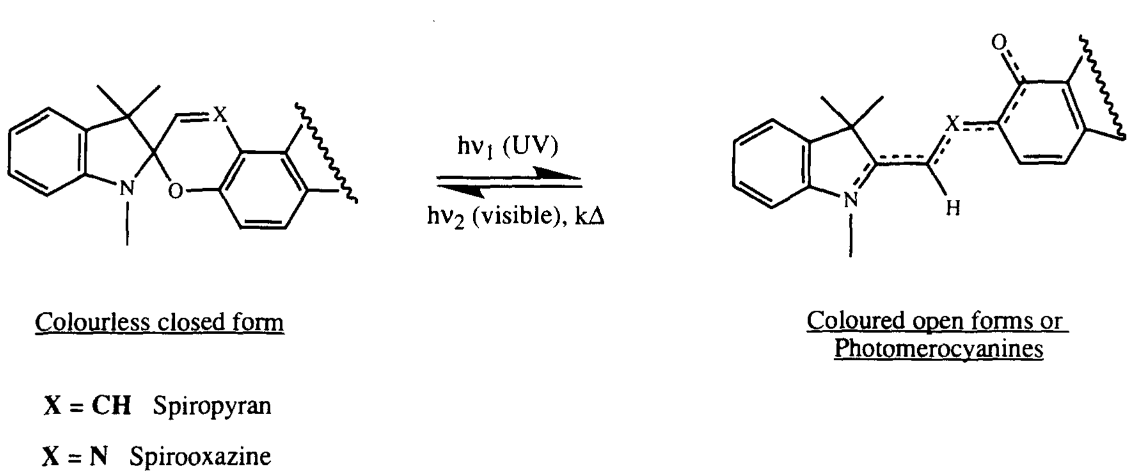


Scheme 1. Photochromic equilibrium between the closed and open forms or photomerocyanines.

During the course of several photodegradation experiments, we have observed a variation with time (generally an increase) of the thermal bleaching rate constant k_Δ, and the purpose of this work was to investigate the possible origins of this observed kinetic variation.

2.1. Photodegradation experiments

As mentioned in the preceding section, the thermal bleaching rate constant generally exhibits an important variation during photodegradation. In order to visualize this phenomenon, some photodegradation results are shown in Table 1: the initial thermal bleaching rate constant $k_{\Delta(A_o)}$ (measured after the first flash) and its variation Δk_Δ (in per cent) after the photodegradation experiment are indicated. The photodegradation and thermal bleaching rate constant measurements are based on the use of a spectrophotometric apparatus called Degraphot [12] described below and illustrated in Fig. 1.

2.1.1. Description of apparatus

The degradation of photochromic molecules is photochemically induced. Thus, for the measurement of the fatigue resistance, we have developed a home-built specific apparatus which simulates the irradiation conditions of daylight exposure: a 250 W xenon arc lamp (XBO Osram) and a Schott WG 295 filter (France) with a cut-off at 280 nm were used.

The Degraphot apparatus measurements are described in terms of the fatigue resistance by the determination of the parameter $t_{A_o/2}$ (time in minutes necessary to reduce the initial colourability A_o to $A_o/2$).

This computer-controlled apparatus, initially designed to monitor and analyse the photodegradation process by continuous xenon lamp irradiation, has also been used to monitor, in detail, the kinetics of thermal decolouration of the photochromic solutions. This kinetic data availability offered by the Degraphot apparatus has been exploited to show that the variation of the thermal bleaching rate constant is a function of the irradiation time (Figs. 2–5, see Section 2.1.2).

The experimental protocol used is shown in Fig. 1. After the initial measurement of the absorbance (A_o) and the thermal bleaching rate constant ($k_{\Delta(A_o)}$) of the photochromic solution after the first flash, the continuous degradation mode is characterized by n sequences of successive bright (T_B) and dark (T_D) periods. At the end of every sequence (T_B–T_D) (shutter closed), a measurement flash is triggered and a kinetic scan is started. Simultaneously, an $I_x = f(t)$ graph is registered (I, intensity; x, rank of the sequence (T_B–T_D)). At the end of the experiment, the conversion of the intensity of absorbance is operated by the software module and the fatigue resistance time $t_{A_o/2}$ (time when $A_o/2$ absorbance is reached) is calculated by an interpolation method.

The kinetic treatment of the $A_x = f(t)$ graph at the end of each cycle (T_B–T_D) gives the value of $k_{\Delta(A_x)}$ corresponding to the time of irradiation. In this way, we obtained $k_{\Delta(A_o/2)}$ relative to the time $t_{A_o/2}$ and calculated the ratio of the k_Δ variation against the initial value $k_{\Delta(A_o)}$. This k_Δ variation is given in per cent by the term Δk_Δ

$$\Delta k_\Delta\ (\%) = (k_{\Delta(A_o/2)} - k_{\Delta(A_o)}) \times 100 / k_{\Delta(A_o)}$$

Table 1
Thermal bleaching rate constant evolution during the photodegradation process (Degraphot photodegradation and kinetic measurements)

Photochomic compound	$t_{A_o/2}$ (min)	$k_{\Delta(A_o)}$ (s^{-1})	$k_{\Delta(A_o/2)}$ (s^{-1})	Δk_Δ (%)	Kinetics
I	515	0.38	2.03	> +100	Significant acceleration
II	125	7.88	13.23	+67	Acceleration
III	22	0.082	0.074	−10	Weak deceleration
IV	7	0.027	0.03	0	No variation

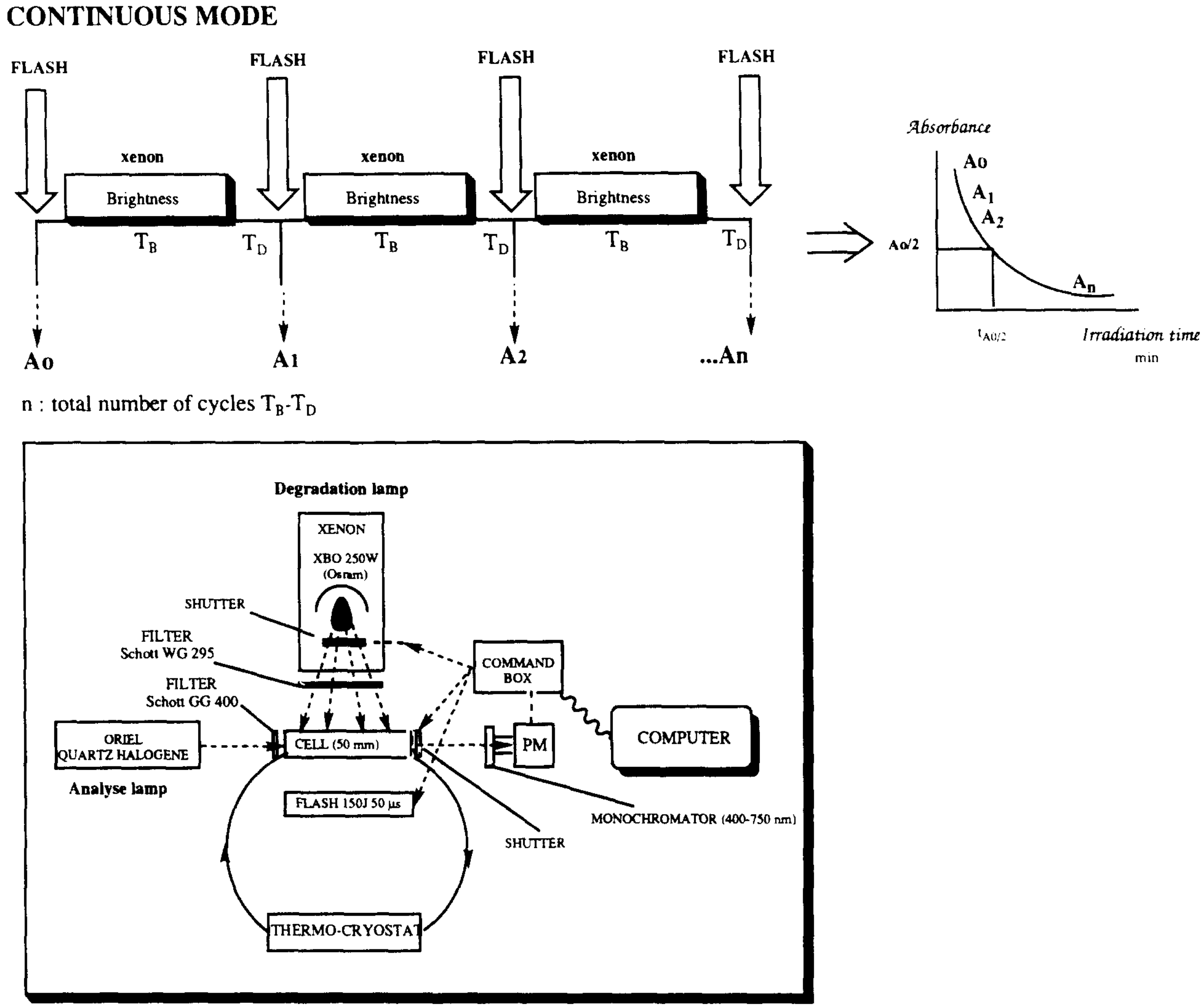


Fig. 1. Description of the continuous degradation mode of the Degraphot apparatus.

2.1.2. Results

In the fixed experimental conditions for the photodegradation measurements (concentration of the photochromic compound $C=0.5\times10^{-5}$ M; solvent, anhydrous toluene (SDS, France); $V=5$ ml; $T=298$ K), 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]naphth[2,1-b][1,4]oxazine] (**I**) exhibits the highest value of the fatigue resistance ($t_{A_0/2}=515$ min) and the most important increase in the decolouration rate constant ($\Delta k_{\Delta I} > +100\%$). For the three other compounds examined, i.e. 1,3-dihydro-7'-nitro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]naphth[2,1-b]pyran] (**II**), 1,3-dihydro-5,6',8'-trimethoxy-1-isopropyl-3,3-dimethylspiro-[2H-indole-2,2'-[3H]benzoxazine] (**III**) and 1,3-dihydro-8'-methoxy-6'-nitro-1,3,3-trimethylspiro[2H-indole-2,2'-[3H]benzopyran] (**IV**), we observed an acceleration ($\Delta k_{\Delta II}=+67\%$), a weak deceleration ($\Delta k_{\Delta III}=-10\%$) and no variation ($\Delta k_{\Delta IV}=0\%$) of the thermal bleaching rate constant k_Δ respectively.

Nevertheless, the tendency to deceleration or no variation is lower than the acceleration generally observed for spirooxazines and spiropyrans [13].

These results are illustrated in Figs. 2–5 and Table 1.

2.1.3. Discussion

These results, together with the kinetic measurements after a single flash (without irradiation) of a solution of the photochromic compound dissolved in a previously degraded photochromic solution, suggest that the decolouration rate constant k_Δ is probably modified by the presence of photoproducts. In order to determine whether this perturbation is associated with the presence of photoproducts originating from the spiro molecule or from the solvent (toluene), we tested a photochromic solution prepared with irradiated toluene. We observed a significant variation of k_Δ. Thus the kinetic variation is not due to the presence of photoproducts originating from the photochromic molecule in the degraded solution, but exclusively due to the photoproduct(s) gener-

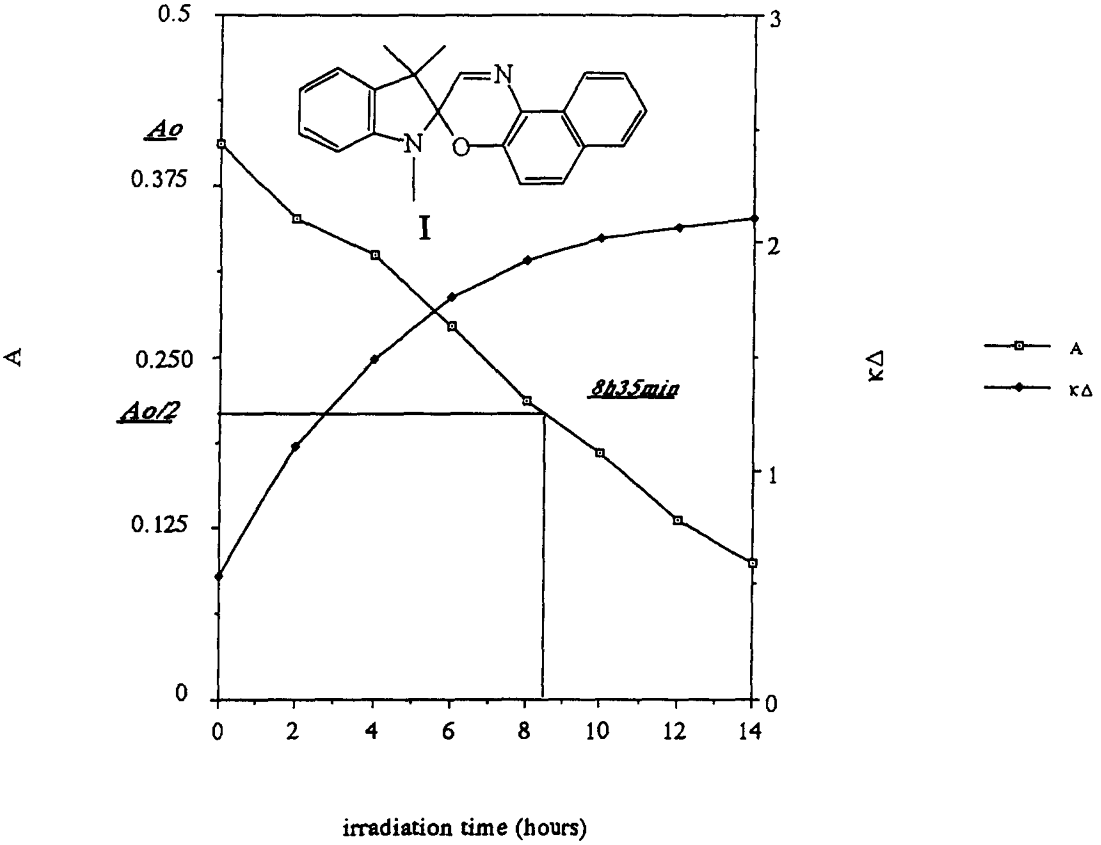


Fig. 2. Variation of the absorbance (A) and thermal bleaching rate constant (k_Δ) as a function of the irradiation time for the spiro[indoline-naphthoxazine] I.

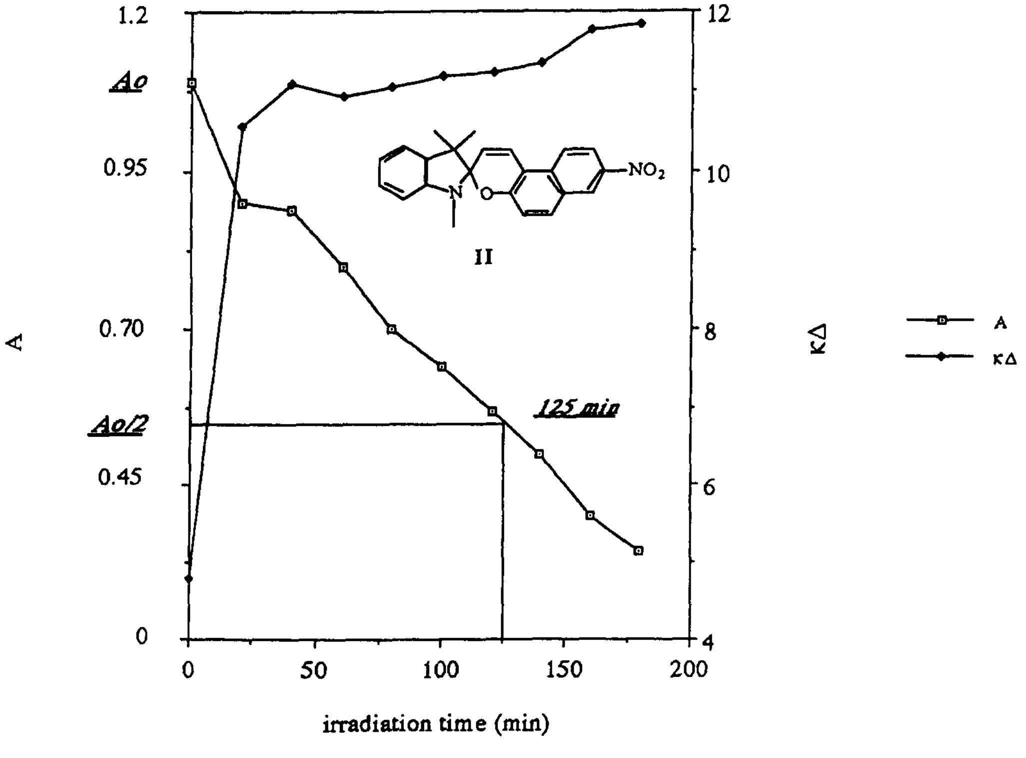


Fig. 3. Variation of the absorbance (A) and thermal bleaching rate constant (k_Δ) as a function of the irradiation time for the spiro[indoline-naphthopyran] II.

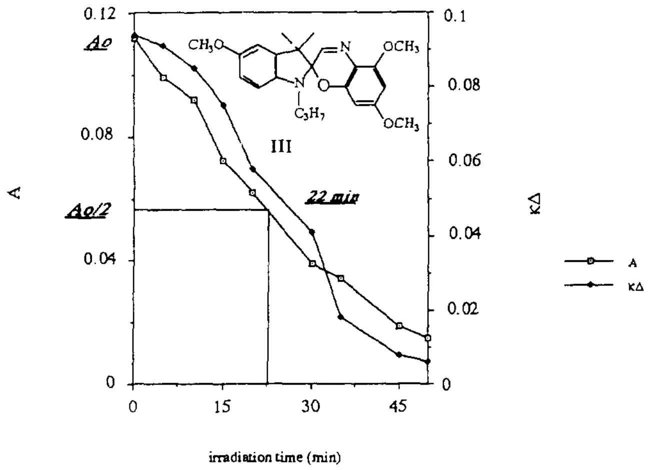


Fig. 4. Variation of the absorbance (A) and thermal bleaching rate constant (k_Δ) as a function of the irradiation time for the spiro[indoline-benzoxazine] III.

ated via the degradation of toluene. We studied two types of oxidized derivative of toluene formed via photodegradation of a contact charge transfer complex [14]: benzaldehyde and benzoic acid, detectable by high performance liquid chromatography (Beckman HPLC Gold system) coupled with a UV-visible 168 diode array detector. The separation system consisted of a C8 RX Zorbax reverse phase column (Rockland Technologies) (25 cm × 4.6 mm) with a gradient of acetonitrile in acidified water (pH 2.9) from 30% to 100% (40 min; 1 ml min^{-1}). In the second part of this work, we report the kinetic results obtained on addition of these different toluene derivatives to the photochromic solution.

2.2. Kinetic study

The kinetic measurement mode (without irradiation) of the Degraphot system [12] is shown in Fig. 6. This software module has been developed to obtain, with high accuracy, the thermal ring closure kinetic constants of the photomerocyanines. In this mode, once the initial absorbance A_0 is obtained, the flash is fired and the software monitors the kinetic curve with a rate set by the user on program request.

In order to process the spectrokinetic data, the estimation of the amplitude and time parameters for monoexponential signals was performed by a classical linear least-squares method [15].

2.2.1. Results

The kinetic results on addition of benzaldehyde and benzoic acid are given in Fig. 7.

Benzaldehyde generates kinetic variation for the spiro compounds (SP) studied and is operative from a concentration of 10^{-4} M. In a first approach [13,16], benzaldehyde was suspected to act as either a photosensitizer or a quencher ($E_T = 300.96$ kJ mol^{-1}) of the triplet excited state of the photomerocyanines (PM) by donor–acceptor energy transfer. Therefore, in addition to the thermal factor, light was proposed to facilitate spiro ring closure

$$\mathrm{SP} \underset{k_\Delta,\ h\nu_2}{\overset{h\nu_1}{\rightleftarrows}} \mathrm{PM}$$

where $k_{\mathrm{decolouration}} = k_\Delta + k_{h\nu_2}$ and $k_{h\nu_2}$ is the ring closure rate constant due to light.

Concerning the energy levels E_T, three possibilities have been envisaged.

(1) $E_T(S^*) > E_T(PM^*)$; $\Delta k_\Delta > 0$ (acceleration)

$$PM^* + {}^3S^* \longrightarrow SP + S$$

where S is the photosensitizer of the spiro ring closure.

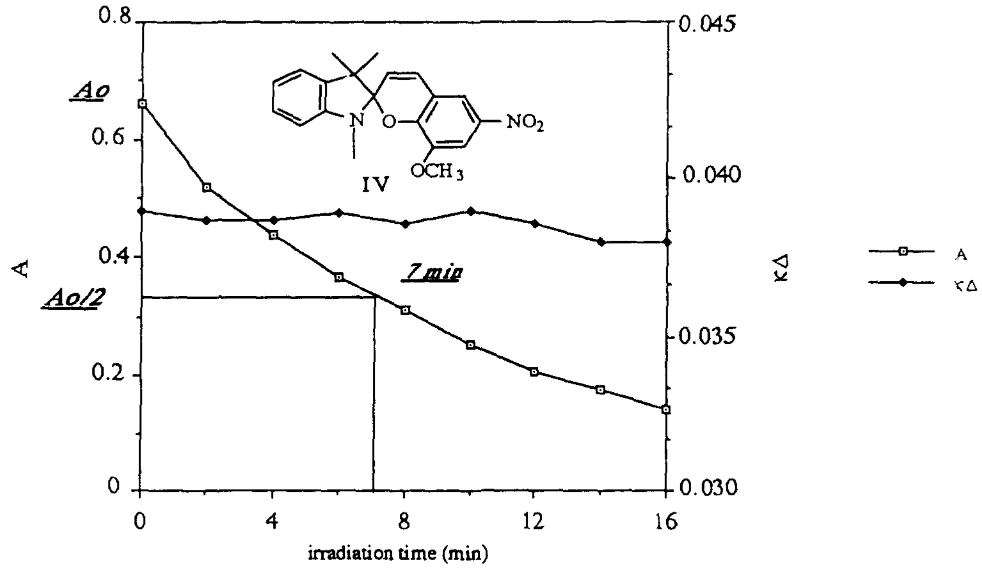


Fig. 5. Variation of the absorbance (A) and thermal bleaching rate constant (k_Δ) as a function of the irradiation time for the spiro[indoline-benzopyran] IV.

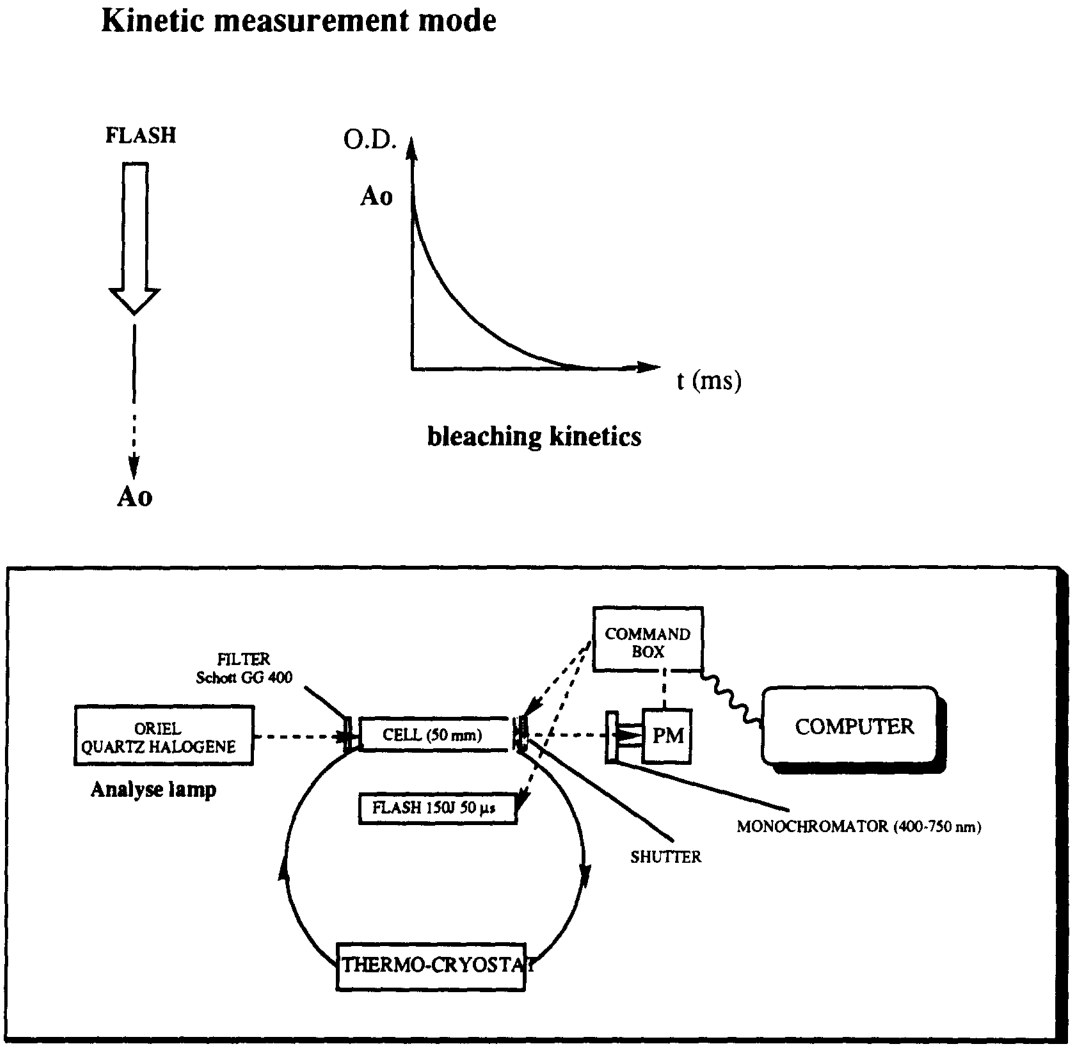


Fig. 6. Description of the kinetic measurement mode of the Degraphot apparatus.

(2) $E_T(S^*) < E_T(PM^*)$; $\Delta k_\Delta < 0$ (deceleration)

$$PM^* + {}^3S^* \longrightarrow PM + {}^1S^*$$

where S is the quencher of the spiro ring closure.

(3) $E_T(S^*) \gg E_T(PM^*)$; $\Delta k_\Delta = 0$ (no effect).

The mechanism of energy transfer between benzaldehyde and the triplet excited state of the photomerocyanine was initially proposed to explain the variation of the rate constant of thermal ring closure. However, this hypothesis was contradicted by the inefficiency of photosensitizers with comparable energy, e.g. benzophenone ($E_T = 286.75$ kJ mol^{-1}), fluorenone ($E_T = 221.96$ kJ mol^{-1}) and diphenylamine ($E_T = 300.96$ kJ mol^{-1}) [17]. In all cases ($10^{-6} < C < 10^{-2}$ M; solvent: toluene, ethanol, acetonitrile) no effect was noticed, with the exception of benzophenone which causes a weak slowing down of the decolouration rate constant of benzoxazine **III** ($C_{\text{benzophenone}} = 1.5 \times 10^{-5}$ M, $\Delta k_\Delta = -10\%$).

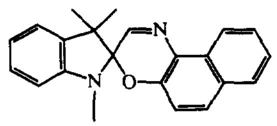
Other experiments with the addition of acid (benzoic acid) yielded similar results to the benzaldehyde effect and were consistent with the sign and range of the k_Δ variation obtained during the photodegradation experiments (Table 1) (acceleration for **I** and **II**; deceleration for **III**). Therefore the results obtained with benzaldehyde could be directly due to the easy oxidation of benzaldehyde to benzoic acid.

Another significant result was the important acceleration obtained with compound **IV** in the presence of benzoic acid (maximum $\Delta k_\Delta > 100\%$, $C_{\text{benzoic acid}} = 10^{-4}$ M). No variation in k_Δ was observed during the photodegradation experiments (Table 1) with this compound, because of the short time of irradiation (7 min vs. 515 or 125 min for compounds **I** and **II**). The degradation of toluene in benzaldehyde and benzoic acid requires prolonged irradiation.

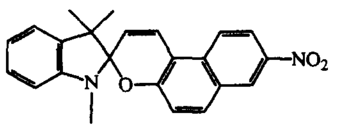
2.2.2. Discussion

The easy oxidation of benzaldehyde to benzoic acid by ambient oxygen is in line with the kinetic variation observed and is supported by experiments with the addition of benzoic acid.

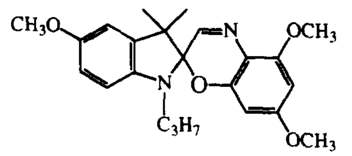
Nevertheless, having excluded a triplet–triplet photosensitizing ability of benzaldehyde or benzoic acid, we used chloroacetic acid (no triplet photosensitizing ability) to



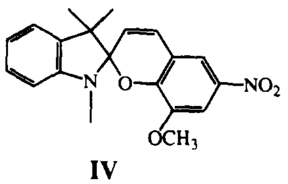
I



II



III



IV

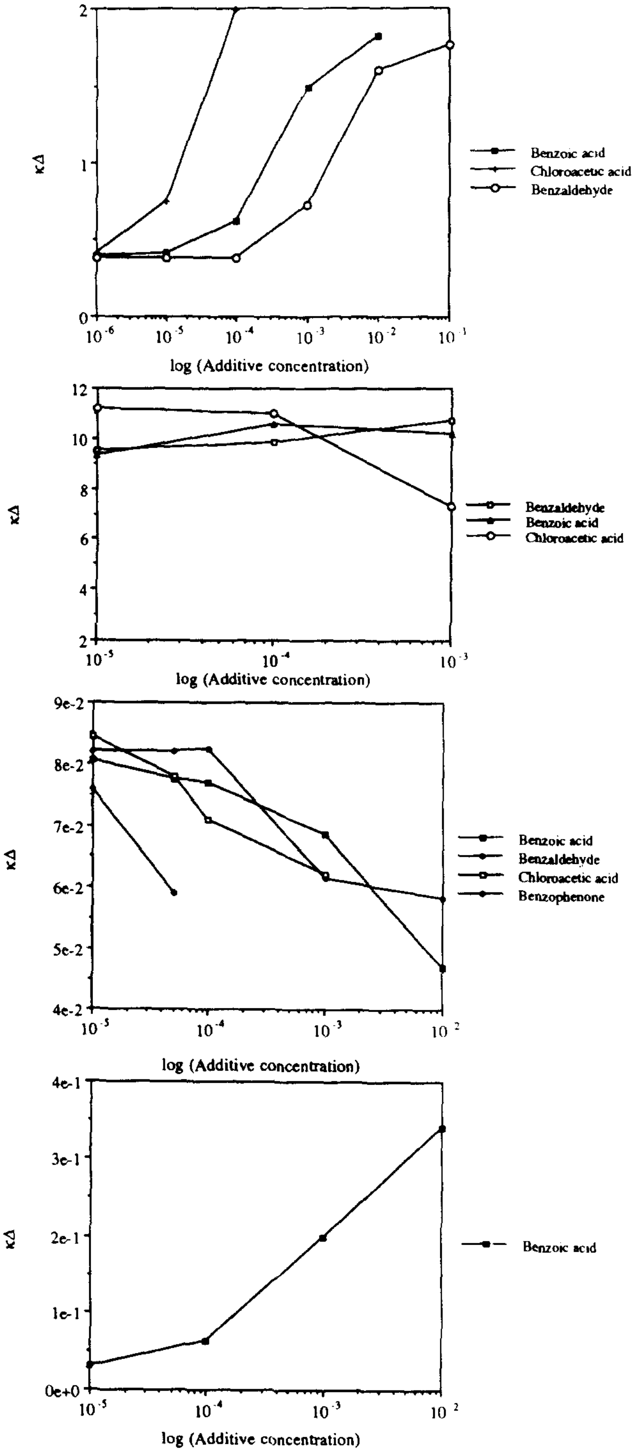
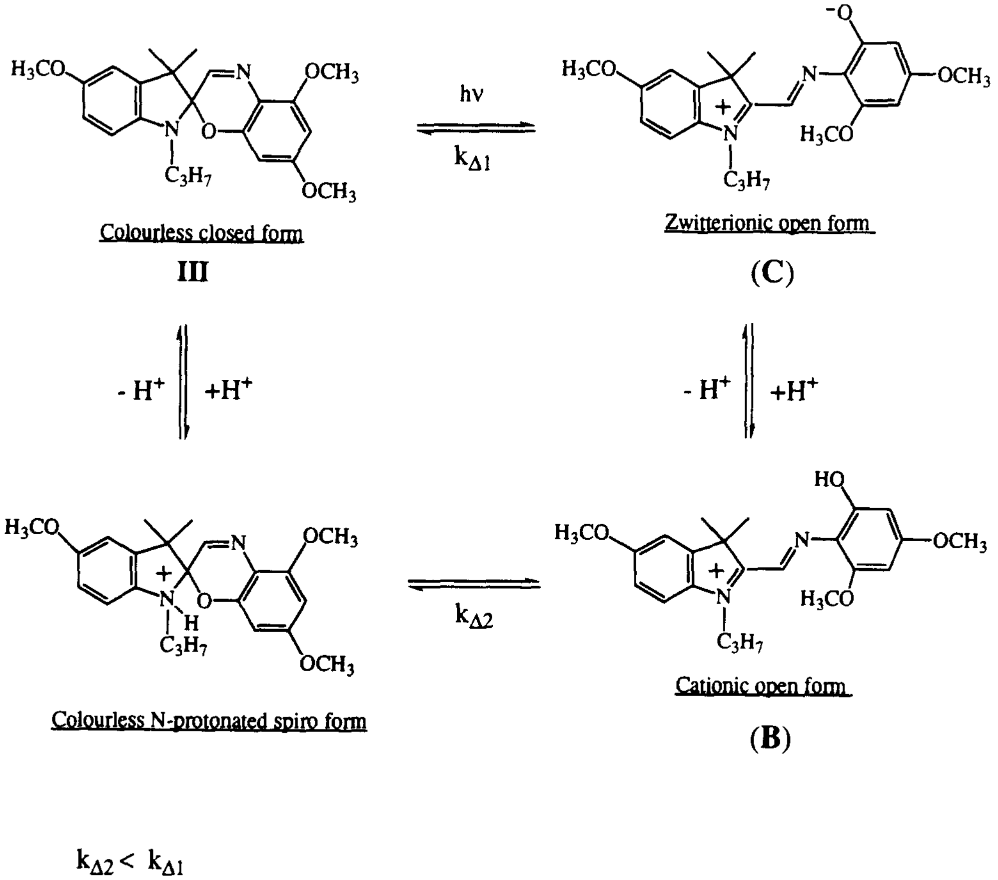


Fig. 7. Variation of the thermal bleaching rate constant (k_Δ) of the photochromic compounds on addition of benzaldehyde, benzoic acid, chloroacetic acid or benzophenone.

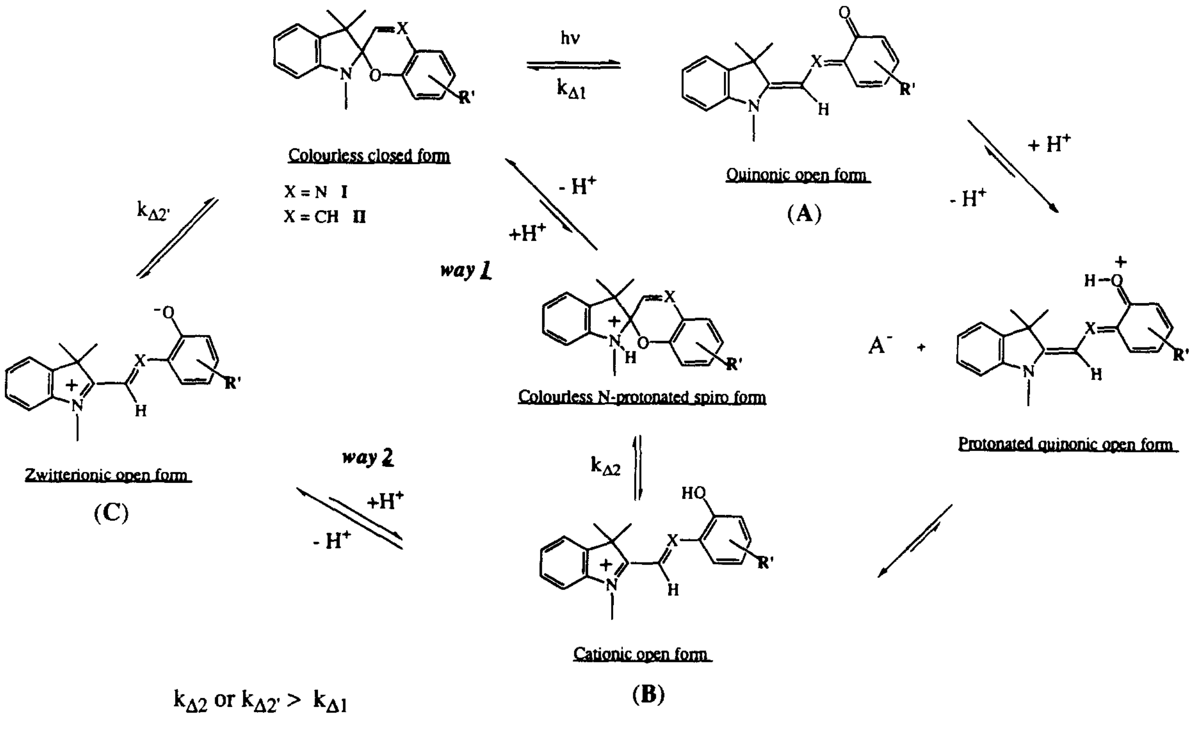
check whether the proton donor properties of acids are involved in this phenomenon. Convincing evidence that the variation of the thermal bleaching rate constant is a function of the strength of the acid resulted from a systematically higher performance of the latter acid vs. benzoic acid for an identical acid concentration. The plots of k_Δ evolution as a function of the additive concentration are presented in Fig. 7 and the corresponding values are summarized in Table 2. On this basis, a simplified classification in terms of the ability of the tested additives to induce kinetic variation can be given: chloroacetic acid > benzoic acid > benzaldehyde.

3. Conclusions

In all cases, chloroacetic acid acts more efficiently on the thermal bleaching rate constant k_Δ than benzoic acid: this



Scheme 2. Mechanism for the deceleration of k_Δ occurring on addition of acid.



Scheme 3. Mechanism for the acceleration of k_Δ induced on addition of acid.

Table 2
Summary of the results of the variation in the thermal bleaching rate constant (k_Δ) in the presence of additives

Photochromic compound (5×10^{-6} M)	Concentration (mol l^{-1}) [a]				Reference Δk_Δ (%) [b]
	Benzophenone	$ClCH_2CO_2H$	Benzoic acid	Benzaldehyde	
I	No effect [e]	10^{-4}	4×10^{-3}	10^{-1}	> +100
II	No effect [e]	10^{-5} (42.25%) [c]	10^{-4} (34%) [c]	10^{-3} (36%) [c]	+67
III	1.5×10^{-5}	10^{-4}	2.5×10^{-4}	5×10^{-4}	−10
IV	No effect [e]		10^{-4} (>100%) [d]		0

Solvent toluene.

[a] Acid additive concentration needed to reach the experimental value of the variation of Δk_Δ (%) observed during the photodegradation experiments.

[b] Observed variation of Δk_Δ (%) during the photodegradation experiments.

[c,d] Maximum value of the variation of Δk_Δ (%) obtained in the presence of acid.

[e] No effect whatever the concentration.

process can be directly associated with the strength of the acid. The pathway of this process needs to be determined.

In Section 1, we reported that the rate of thermal reversion of photomerocyanines to spiro compounds is controlled by a large number of factors, one of the most important being the matrix or liquid solution in which the photochromic organic molecule is dissolved. For example, under appropriate acidic conditions [18], the spiro form can be transformed into an open cationic form (**B**) through the zwitterionic merocyanine form (**C**). In these acidic conditions, an acid–base equilibrium is established between the two open forms (**B** and **C**), which competes (k_{Δ_2}) and slows down the classic spiro ring closure (k_{Δ_1}) observed with benzoxazine **III** (Scheme 2).

Concerning the acceleration of the rate constant k_Δ observed with **I** and **II** (Table 1), Kellmann et al. [5,6] have described the effect of solvent polarity on the rate of thermal reversion of some substituted photomerocyanines. They have established that the rate of decolouration of **I** increases with increasing solvent polarity ($k_{\Delta I} = 38\times10^{-2}$ M in toluene vs. 140×10^{-2} M in dimethyl sulphoxide and 67×10^{-2} M in ethanol), this variation being correlated with a predominant quinoidal structure of the open form generated on irradiation (positive solvatochromism).

By a similar pathway (Scheme 3), we suppose that the photomerocyanines are changed in the presence of a proton donor. In toluene solution, quinonic open forms (**A**) are formed predominantly. The protonation of this species gives rise, by electron shifts, to a cationic open form (**B**) which, by previous deprotonation (pathway 2), could lead to a double-charged unstable zwitterionic open form (**C**). This latter ionic form can proceed to a faster spiro ring closure (k_{Δ_2}.) than the initial uncharged quinonic form (**A**, k_{Δ_1}) in an apolar aprotic solvent (toluene). The deprotonation can also follow the accelerated (k_{Δ_2}) spiro ring reclosure (pathway 1).

From this discussion, the importance of the nature of the open forms generated on irradiation in inducing, at the same temperature, rate constant variations can be seen.

4. Experimental details

The photochromic compounds (**I**, **II**, **III** and **IV**) were prepared by the Group "Photochromes Organiques-Matériaux" URA CNRS 1320, Faculté de Luminy, Marseille, France. Compound **III** was prepared at PPG Industries Laboratory, Pittsburg, USA.

For the Degraphot [12] experiments, the photochromic compounds (**I**, **II**, **III** and **IV**) ($C = 0.5\times10^{-5}$ M) and benzaldehyde, benzoic acid and chloroacetic acid (commercially available, Aldrich) were dissolved in 5 ml of anhydrous toluene (SDS, France).

Both of the measurement modes used (Figs. 1 and 6) were piloted by programmes developed in house with the partnership of P. Levoir, R. Dubest and J.J. Meyer (Laboratory ITODYS, URA 34, Université de Paris VII, France).

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