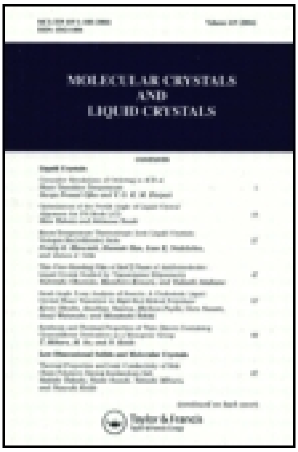

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Kinetic Analysis of the Photochromic Behavior of a Naturally Occurring Chromene (Lapachenole) Under Steady Irradiation

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KINETIC ANALYSIS OF THE PHOTOCHROMIC BEHAVIOR OF A NATURALLY OCCURRING CHROMENE (LAPACHENOLE) UNDER STEADY IRRADIATION

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Abstract The photokinetic behavior of a naturally occurring chromene, lapachenole (2,2-dimethyl-6-methoxy-7,8-benzo(2H)chromene, ***Ch***), has been investigated by using monochromatic irradiation in the UV and visible ranges. Two colored photoproducts were identified: one is thermoreversible, the other is thermostable and photoreversible. The quantum yields of the color-forming and color-bleaching photoreactions were determined by a spectrokinetic method. The kinetic parameters of the thermal steps were measured (285 - 325 K). The sensitized color-forming reaction was also investigated, using thioxantone as a triplet sensitizer. A plausible reaction mechanism is proposed.

INTRODUCTION

Interest in the photochromic behavior of chromenes was first addressed by Becker and coworkers.[1-6] These molecules, upon UV irradiation, yield open colored forms, the structure of which was shown to be an *o*-quinone-allide.[2] The thermal stability of these photoproducts markedly depends on the structure and substituents.[1]

The photochemistry of 2,2-dimethyl-6-methoxy-7,8-benzo(2H)chromene, ***Ch***, was previously investigated in a rigid matrix at 77 K[1,4] and by microsecond and nanosecond flash photolysis techniques.[6] Theoretical calculations on the electronic transitions were also performed.[5]

In this paper, the photochromic reaction of ***Ch*** is investigated under steady irradiation in a temperature range (285-325 K) close to room temperature. The photokinetic method applied to this system allows to gain more insight into the reaction mechanism and the nature and properties of the photoproducts.

MATERIALS AND METHODS

The photochromic compound studied, lapachenole, was a gift from J. Morgan,[4] Forest Products Research Laboratory, England. The solvent was acetonitrile/water (85/15, v/v).

Absorption spectra were recorded on a Perkin-Elmer Lambda 16 or a Beckman diode array DU 7500 spectrophotometers. Temperature in the range 285-325 K was controlled by a cryostat (Oxford Instruments).

The irradiation wavelengths (λ_{exc} = 381 and 452 nm) were selected from the emission of a 150 W Xe lamp filtered by a monochromator (Jobin-Yvon H10 UV)). The light intensity (typically, 6×10^{-7} einstein dm^{-3} s^{-1}) was determined using potassium ferrioxalate actinometry. The light exposure of the sample (1-cm path cell, 1 cm^3 of solution) was carried out in the spectrophotometer holder at right angles to the analysis light. The color-forming reaction was followed up to photostationary state attainment.

The kinetics of the thermal back reaction were recorded following the color-bleaching of the irradiated solution, immediately after having removed the irradiating source. After complete thermal-bleaching, the photo-bleaching was followed at the maximum of the color-band under steady irradiation with visible light (λ_{exc} = 452 nm).

The color-forming reaction sensitized by thioxantone, ***TX***, ([***TX***] = 6×10^{-4} mol dm^{-3}) was studied varying the ***Ch*** concentration in the range 3.9×10^{-5}-1.1×10^{-4} mol dm^{-3} by using 404 nm irradiation wavelength (chosen as a compromise of no-absorption by ***Ch***, sufficient absorption by the sensitizer and minimum absorption by ***B***).

RESULTS

The colorless ***Ch*** solution turns yellow upon UV irradiation and a new band is observed in the visible (λ_{max} = 452 nm). Its intensity, at the photostationary state, markedly increases with decreasing temperature. A typical time-course of the color-forming reaction of ***Ch*** is illustrated in FIGURE 1. The color-forming kinetics are formally described by the biexponential function of Equation (1), where A represents the absorption at the color maximum wavelength (452 nm) and a, b, α and β are parameters, determined by a fit procedure, which depend on the absorbed light and temperature.

$$A = a(1 - e^{-\alpha t}) + b(1 - e^{-\beta t}) \qquad (1)$$

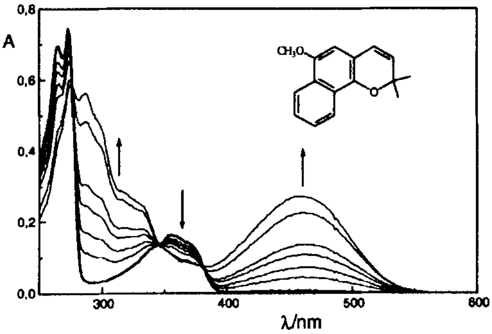
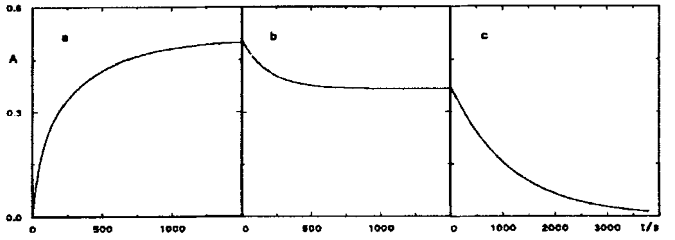


FIGURE 1 Time-course of the spectral changes during the color-forming reaction of ***Ch*** in acetonitrile/water (85/15, v/v) at 300 K.

After removing the irradiating source, the solution partially bleaches, leaving a residual visible absorption. The initial ***Ch*** spectrum is restored completely only upon irradiation with visible light. The absorbance changes observed in the color-band at 452 nm are illustrated in FIGURE 2.



UV on light off Visible on

FIGURE 2 Absorbance changes at λ = 452 nm under UV irradiation (λ_{exc} = 381 nm, a), in the dark (b) and under visible irradiation (λ_{exc} = 452 nm, c).

This behavior indicates the formation of two photoproducts, which possess very close absorption spectra in the visible, but different thermal stabilities. They are assigned to two isomers (*o*-quinone-allide structures), originated from the electrocyclic ring-opening due to the rupture of the O-C_2 bond of ***Ch***. One (***A***) of these isomers spontaneously back-isomerizes in the dark, the other (***B***) reconverts to ***Ch*** only upon irradiation. The kinetic of the thermal bleaching follows a monoexponential law (Equation (2)), where k_A, the

$$A = a' e^{-k_A t} + R \qquad (2)$$

bleaching rate parameter of the photoproduct ***A***, is determined by a fit procedure. The residual absorption, R, is due to the thermostable photoproduct ***B***. The activation energy of the thermal bleaching, determined from the Arrhenius plot in the 285-325 K temperature range, is 70 kJ mol^{-1}.

Due to its thermal stability, the isomer ***B*** could be isolated from the irradiated solution by HPLC and its spectrum (FIGURE 3) and molar absorption coefficient (ε_{max} = 12000 ± 1000 $dm^3\ mol^{-1}\ cm^{-1}$) were determined.

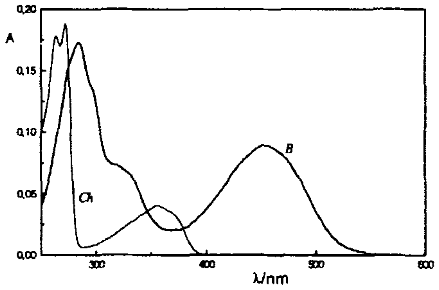


FIGURE 3 Spectrum of ***B*** and spectrum of ***Ch***, completely recovered after visible irradiation of the solution of ***B***.

The photobleaching of ***B*** (FIGURE 2c) follows the kinetic Equation (3):

$$- dA_B/dt = \varepsilon_B \Phi_{-B} I^{\circ}(1 - 10^{-A_B}) \qquad (3)$$

The quantum yield (Φ_{-B}) of this process, determined at several temperatures from the intercept (or slope) of the linear plots - dA_B/dt vs. 10^{-A_B}, is shown in FIGURE 4. It increases with temperature, attaining a constant limit value (0.45 ± 0.05) above 310 K (FIGURE 5). By applying an Arrhenius-type treatment to the increasing Φ_{-B} region ($T \leq$ 310 K), an activation energy of 62 kJ mol^{-1} was obtained. This value is close to the activation energy of the thermal bleaching of ***A***.

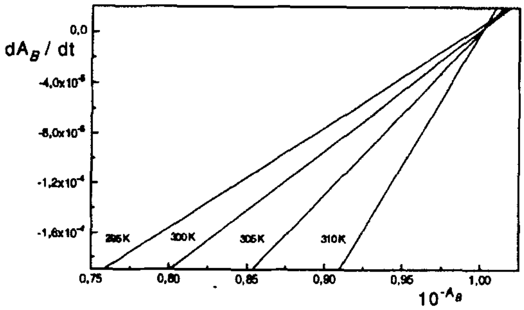


FIGURE 4 Temperature effect on the photobleaching rate

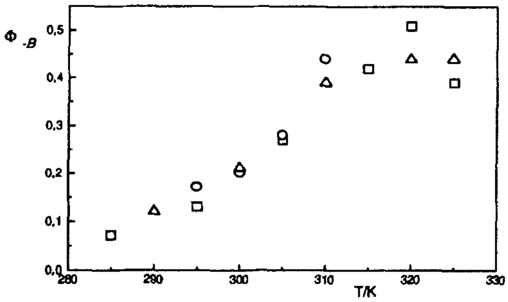


FIGURE 5 Temperature effect on Φ_{-B} (three independent runs).

The opening reaction is photosensitized by thioxantone, TX, (E_T = 270 kJ mol^{-1}, $\Phi_T = 1$, τ_T = 10 μs, where the subscript T refers to the triplet state T_1), but not by sensitizers with lower triplet energy, such as fluorenone and biacetyl. At the photostationary state, the conversion percentage is close to unity. The photoproduct is mainly ***B***; minor amounts of ***A*** are also observed at the end of irradiation.

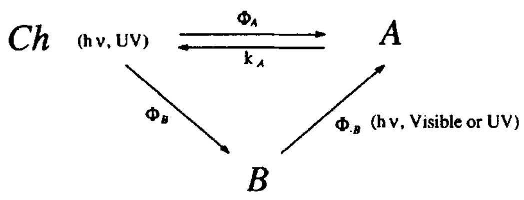
The quantum yield of the sensitized reaction (Φ_S) was determined from the initial reaction rate (Equation (4)):

$$\Phi_S = \frac{(dA_B/dt)_{t\to 0}}{I^o \varepsilon_B (1 - 10^{-A_S})} \qquad (4)$$

The Φ_S values do not follow the Stern-Volmer equation; the quantum yield decreases with increasing the ***Ch*** concentration. The maximum Φ_S value is 0.52 ± 0.05.

MECHANISM AND KINETICS

In order to set up the kinetic equations and thus to determine the quantum yields of the photoreactions, a reasonable mechanism must be postulated. Based on the above findings, the following reaction scheme is tentatively proposed:



Scheme 1

Upon direct UV irradiation, ***Ch*** gives ***A*** (which decays thermally) and ***B***, which photochemically reconverts to ***Ch*** through ***A***. At the stationary state, all three species (***Ch***, ***A***, ***B***) are present. This Scheme is mainly based on the thermal behaviour of ***A*** and ***B*** and the closeness of the activation energies of the ***A*** → ***Ch*** thermal bleaching and the ***B*** → ***Ch*** photochemical bleaching which suggests that the latter process occurs through ***A***. The thermal barrier to the ***A*** → ***Ch*** closure constitutes a bottleneck to the ***B*** → ***A*** → ***Ch*** process at low temperature, but not at higher temperature (FIGURE 5). However, an activated path not involving ***A*** cannot be excluded. Following Scheme 1, the color-forming rate on direct UV irradiation of ***Ch*** is given by Equation (5):

$$dA/dt = dA_A/dt + dA_B/dt = \{I_{Ch}\varepsilon_A\Phi_A - k_A A_A + I_B\varepsilon_A\Phi_{-B}\} + \{I_{Ch}\varepsilon_B\Phi_B - I_B\varepsilon_B\Phi_{-B}\} =$$
$$I^\circ F\varepsilon' [\boldsymbol{Ch}](\varepsilon_A\Phi_A + \varepsilon_B\Phi_B) + I^\circ F\varepsilon' [\boldsymbol{B}]\,\varepsilon_A\Phi_{-B} - I^\circ F\varepsilon' [\boldsymbol{B}]\,\varepsilon_B\Phi_{-B} - k_A A_A \tag{5}$$

$F = [1 - \exp(-2.3A')]/A'$ is the fotokinetic factor;[7,8] A' is the total absorbance at $\lambda_{exc} = 381$ nm (extinction coefficient ε'; isosbestic point where F is a constant). By substituting: $[\boldsymbol{Ch}] = [\boldsymbol{Ch}]_o - [\boldsymbol{A}] - [\boldsymbol{B}] = [\boldsymbol{Ch}]_o - A_A/\varepsilon_A - A_B/\varepsilon_B$, Equation (6) is obtained:

$$dA/dt = I^\circ F\varepsilon' [\boldsymbol{Ch}]_o \{\varepsilon_A\Phi_A + \varepsilon_B\Phi_B\} - \{I^\circ F\,\varepsilon' (\Phi_A + \varepsilon_B/\varepsilon_A\Phi_B) + k_A\}A_A -$$
$$- \{I^\circ F\,\varepsilon' (\varepsilon_A/\varepsilon_B\Phi_A - \varepsilon_A/\varepsilon_B\,\Phi_{-B} + \Phi_B + \Phi_{-B})\}A_B = C - D\,A_A - E\,A_B \tag{6}$$

where C, D and E are constant parameters and the instantaneous A_A and A_B absorbances can be replaced by the experimental time-dependent terms of Equation (1). Integration yields Equation (7):

$$A = Da/\alpha + Eb/\beta + (C - Da - Eb)t - Da/\alpha e^{-\alpha t} - Eb/\beta e^{-\beta t} = a(1 - e^{-\alpha t}) + b(1 - e^{-\beta t}) \quad (7)$$

from where:

$$C = a\alpha + b\beta \qquad D = \alpha \qquad E = \beta \quad (8)$$

The unknown parameters (ε_A, Φ_A, Φ_B, Φ_{-B}) are obtained from Equations (8) and the photostationary state conditions. Φ_{-B} was also independently determined from the photobleaching of ***B*** under visible irradiation (Equation (3)). The closeness of the values obtained supports the scheme proposed as well as the photokinetic method used. The intersystem crossing yield of ***Ch*** (Φ_{ISC}) is obtained by assuming that ***B*** originates from the triplet upon both direct and sensitized excitation ($\Phi_{ISC} = \Phi_B/\Phi_S$). The sum $\Phi_A + \Phi_{ISC}$ approximately accounts for all the absorbed quanta.

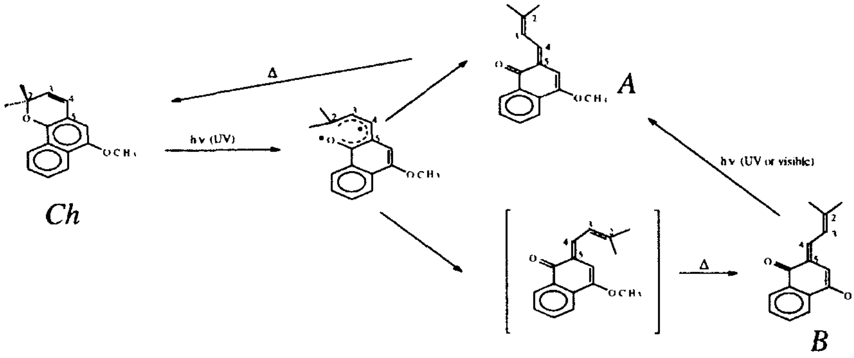
TABLE I Photokinetic parameters

$\varepsilon_A = 3000 \pm 500$ dm^3 mol^{-1} cm^{-1}	$\varepsilon_B = 12000 \pm 1000$ dm^3 mol^{-1} cm^{-1}
$\Phi_A = 0.8 \pm 0.1$	$\Phi_B = 0.08 \pm 0.02$
k_A (s^{-1}) = 0.016 ± 0.002 (310 K)	$\Phi_{-B} = 0.40 \pm 0.1$ ($\lambda_{exc} = 381$ nm) $= 0.45 \pm 0.05$ ($\lambda_{exc} = 452$ nm)
E_A (kJ mol^{-1}) = 70 ± 5	E_{-B} (kJ mol^{-1}) = 62 ± 10
$\Phi_S = 0.52 \pm 0.05$ ($\lambda_{exc} = 404$ nm)	Φ_{ISC} (***Ch***) = 0.15 ± 0.1

CONCLUDING REMARKS

The photochemical ring-opening reaction of ***Ch*** is a two-way process, which yields two isomeric photoproducts. One of them (***A***) is a metastable species which can be detected under steady irradiation and decays thermally to ***Ch***; the other, ***B***, is a thermally stable molecule and therefore it could be isolated. After the C_2-O cleavage, the first species produced without change in nuclear coordinates is a very short-lived diradical, where the

C-C bonds originally in the pyran ring are no longer pure single or double bonds (Scheme 2). In a fluid solution, at room temperature, the formation of stable (or meta-stable) isomers requires twisting around some C-C bond, that is, around C_3-C_4 or C_4-C_5. For chromene, taken as a model molecule, excited-state potential-energy curves (computed using INDO/2)[9] indicate that both paths are allowed in the S_1 and T_1 states. In the present case, twisting around C_3-C_4 yields the isomer *A*, which thermally reconverts to ***Ch*** by rotating around a quasi-single bond, while twisting around C_4-C_5 leads to a hindered isomer (in bracketts) which is stabilized by rotating around C_3-C_4. ***B*** is thermally stable; by light absorption it converts to *A* (rotation around a double bond) and then back to ***Ch*** thermally.



Scheme 2

Comparing direct and sensitized reactions indicates that twisting around C_4-C_5 in the diradical is favored in the triplet state (230 kJ mol^{-1} < E_T < 270 kJ mol^{-1}).

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