

PHOTOPHYSICS, PHOTOCHEMISTRY AND KINETICS OF PHOTOCHROMIC 2H-PYRANS AND CHROMENES

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(Received September 19, 1985)

Summary

Nine naturally occurring and synthetic chromenes and 2H-pyrans (oxo and sulfo) derivatives have been examined using microsecond and nanosecond laser flash techniques. Triplet transients have only been observed for the coumarin-substituted chromenes (xanthyletin and seselin). Photochromism of the coumarin-substituted chromenes arose dominantly via an excited triplet state in about 800 ns. For the other chromenes and 2H-pyrans, the colored forms arose only from an excited singlet state and subnanosecond rise times were observed. Fluorescence lifetimes have been determined for some chromenes at room temperature as well as 77 K. For xanthyletin, a fluorescence lifetime of less than 30 ps at 295 K in hexane was observed.

1. Introduction

The photochromism of pyrans and chromenes as well as their emission properties have been extensively studied earlier by Becker and coworkers [1 - 4]. The structure of the colored form was shown to be an *o*-quinone-allide [2].

The photochemical reaction of those compounds were mostly studied at 77 K in diethyl ether-isopentane-ethyl alcohol (EPA) matrices [3] but, to our knowledge, no attempt has been made to study both the photophysics and the photochemistry of the chromenes by laser flash techniques at room temperature.

Nanosecond (about 1 - 800 ns) and microsecond (about 0.5 - 400 μ s) laser flash spectroscopy were employed to identify the photophysical path involved in the photochemistry of nine naturally occurring and synthetic chromenes and 2H-pyran derivatives. Also, some fluorescence lifetimes were determined.

It is worth pointing out that the indolinospiropyrans are composed of an indoline moiety and a chromene moiety where the electronic wavefunctions are essentially orthogonal and their spectra are composed of transitions

essentially isolated on the separate halves [5]. Also, it has been shown that energy transfer can occur between the two halves [5] so that the results of this study will be pertinent to the photophysics and photochemistry of the indolinospiropyrans. The indolinospiropyrans will be considered in a later paper.

2. Experimental details

All compounds were synthesized and purified as described previously [3, 4]. All the solvents used were spectrograde, and were kept over 3A molecular sieves and used without further purification. The 2-methyltetrahydrofuran and 3-methylpentane were fractionally distilled over sodium and kept over molecular sieves prior to the low temperature emission studies. Absorption spectra were recorded on a Hewlett-Packard 8450 A UV-visible spectrophotometer.

The microsecond laser flash experiments were carried out using a Q-switched Nd-YAG laser (11 ns pulse width). The rise time of the system is about 0.4 μ s. The excitation sources were the 355 nm third harmonic or the 266 nm fourth harmonic. The kinetic absorption spectrometer used to detect the optical density changes Δ OD after excitation has been described previously [6]. All lifetimes are \pm 10%. The output of the laser was 50 mJ and the energy of the beam was controlled by the use of wiremesh screens. The common chosen energies were in the range from 1 to 5 mJ. The solutions were placed in rectangular quartz cells with 5 mm path lengths along the monitoring light, and they were degassed by bubbling nitrogen through during each experiment. Also, oxygen was used to determine particularly the presence of triplet excited state transients.

The nanosecond experiments used the third and fourth harmonics generated from a mode-locked Nd-YAG laser (200 ps; full width at half-maximum (FWHM), 13 mJ). The kinetic absorption spectrometer consisted of a continuously operating 150 W xenon arc lamp, two electromechanical shutters, quartz lenses, a target cell holder, a Spex Minimate monochromator and a photomultiplier tube (Hamamatsu R 928). The detector output waveforms were processed by a fast Tektronix R 7912 digitizer and computer combination (PDP 11/70). The rise time of the detection system (photomultiplier tube and digitizer) was 1 ns.

The fluorescence lifetimes were determined by a photon-counting technique. The excitation was done by an Nd-YAG mode-locked laser pumping, at 532 nm (60 ps pulse), a dye laser containing Rhodamine B. The excitation wavelength tuned was 600 nm and then this was frequency doubled (average power, about 1 μ W). The response time of the photon-counting detection system was 300 ps FWHM. In certain cases, deconvolution permitted the lower limit of the decay time of the fast signals to be reduced to about 100 ps.

For xanthyletin, we measured the fluorescence lifetime using 355 nm excitation (30 ps FWHM) of a mode-locked Nd-YAG laser. The detection of

TABLE 1
Photochromism of 2*H*-pyrans and chromenes

Compound ^a	λ_{\max} (nm) for uncolored absorption ^b	Longest λ_{\max} (nm) for colored form ^b
<i>2H</i> -pyrans		
1	320	390
2	340	390
3	350	410
<i>Chromenes</i>		
4	310	410, 510
5	357	460
6	360	430
7	363	460, 490
8	346	380, 590
9	330, 345	370, 500, 570

^aFor structures, see text.

^bIn ethanol, 295 K.

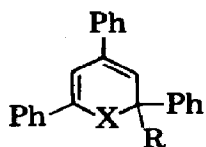
the emission was performed by a Hamamatsu streak camera system with a time resolution of 10 ps.

3. Results and discussion

Table 1 gives data on the absorption spectral properties of the chromenes and 2*H*-pyrans and their photocolored forms.

3.1. 2*H*-pyran, 2*H*-thiopyran and 2*H*-benzopyran (chromene) derivatives

The irradiation of 1, 2 and 3



1: X ≡ O, R ≡ CH₃

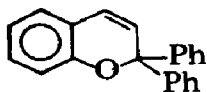
2: X ≡ O, R ≡ -CH₂Ph

3: X ≡ S, R ≡ -CH₂Ph

was done at 355 nm (11 ns pulse; about 1 mJ) in a nitrogen-degassed ethanol solution. In all cases, we observed coloration immediately after the pulse. The absorption spectra of the colored forms are similar to those obtained at 77 K in the EPA matrix in the steady state experiment [3, 4]. No other transients were observed. The 2*H*-pyran 1 was seen to undergo very little photochemistry. The main absorption maximum of the colored form was at about 390 nm. With a similar extinction coefficient assumed, compounds 2 and 3 gave photoproducts in much higher yield, maximizing respectively at 390 nm and 410 nm. The 2*H*-pyran photoproduct is stable over 400 μ s while

the thiopyran thermally closes back to the original compound with a lifetime of 240 μs . The formation and spectra of the colored forms were not affected in any manner by the presence of oxygen in place of nitrogen. The photochemical path is believed to be via an excited singlet state on the basis of the absence of any observable triplet and the fact that the changes ΔOD in optical density on formation of the colored form were unaffected by the presence of oxygen.

A 2*H*-benzopyran (chromene) which has been extensively studied as its 2,2-diethyl-substituted form as a demonstration of the vibronic effect in photochemistry [7] was here studied in its 2,2-diphenyl-substituted form 4:



4

Irradiation of an ethanol solution of 4 at 266 nm (about 1 mJ; 11 ns pulse) resulted in the formation of a colored form with main bands of absorption at 410 nm (the most intense) and 500 nm. The rise time was less than 400 ns (the detection limit) (Fig. 1). No other transient was detected. The colored form showed no decay up to 400 μs and oxygen had no effect on the formation rate or the ΔOD spectrum of the colored form. We also examined compound 4 in a nanosecond laser flash experiment where irradiation was done at 266 nm (13 mJ; 200 ps FWHM). We monitored the kinetics of formation of the colored form at 410 and 500 nm and the rise time was shorter than the rise time detection limit of about 1 ns. On the basis of the absence of an observable triplet, the lack of oxygen quenching of formation of the colored form and the fast rise time, we believe that the opened quinoid form arises via an excited singlet state on the picosecond time scale (and is stable on the microsecond time scale).

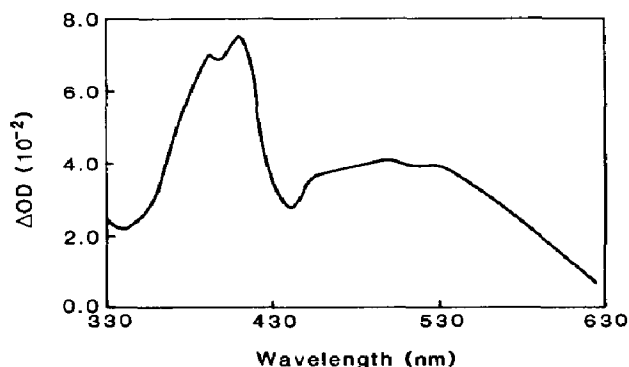
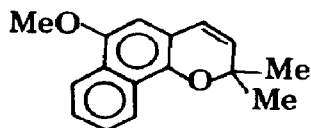


Fig. 1. Transient absorption spectrum (ΔOD spectrum) of 4 in ethanol recorded 1 μs after a 266 nm laser flash.

3.2. Benzochromenes Lapachenole (5)



5

was previously studied in EPA and 3-methylpentane at 77 K. A colored species was observed after irradiation and even different isomeric forms were found by warming the solution of the colored form produced at low temperature [3]. Irradiation at 355 nm (11 ns; 1 - 2 mJ) in a nitrogen-degassed solution of **5** gave a colored form with a maximum absorption at 460 nm and two shoulders at 430 and 490 nm (Fig. 2). This spectrum was very similar to that observed in the steady state experiment at 77 K in EPA where the colored form gave a structured spectrum with three bands at 440, 470 (maximum) and 500 nm. The colored form, which is assigned to be the opened

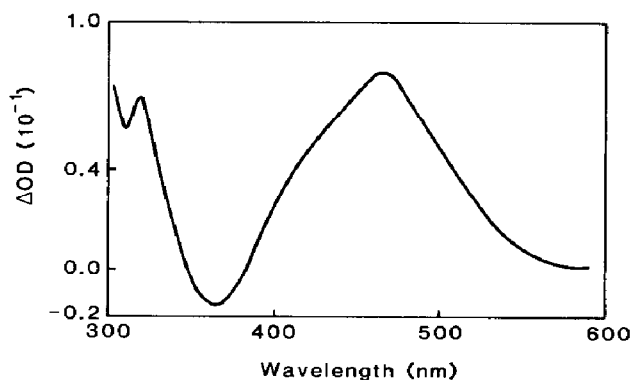
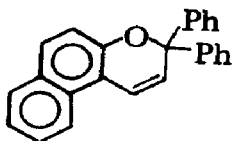


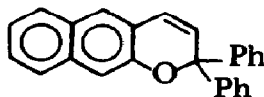
Fig. 2. Transient absorption spectrum (ΔOD spectrum) of **5** in ethanol recorded 1 μs after a 355 nm laser flash.

quinoid form as before, was produced in less than the detection limit of about 400 ns and did not decay for up to about 400 μs . Oxygen had no effect on either the formation rate or the ΔOD spectrum of the colored form. A nanosecond experiment was done with irradiation at 355 nm (13 mJ pulse; 200 ps) and monitoring at 460 nm. We observed a rise time of the colored species of 10 ns. No other transient was detected.

For a comparison, we studied two other benzochromenes, **6** and **7**:

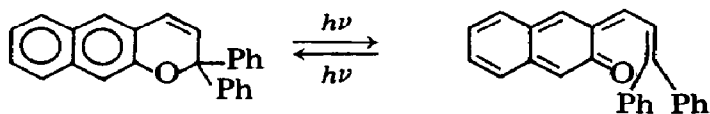


6



7

The chromene 6 gave a photoproduct in less than 400 ns after irradiation at 355 nm (11 ns; about 2 mJ pulse), maximizing at 430 nm. No oxygen quenching was observed and the colored form was stable to above 400 μ s. The naphthochromene 7 gave a photoproduct in less than 400 ns with two peaks at 460 and 490 nm which decayed in 3 - 4 ms. Oxygen had no effect on the results. Compound 7 is interesting because of the absence of a benzene ring moiety in the colored product compared with 5 and 6:

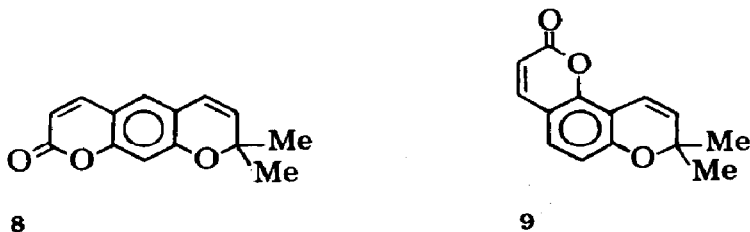


No other transient was seen for either compound 6 or compound 7.

We believe that the colored forms in all cases arise from an excited singlet state on the basis of the absence of an observable triplet, the lack of oxygen quenching and the fast rise time of the colored form as found for 5. Also, for these benzochromenes, the quantum yields of formation of the colored forms appear to be high. No or very little emission was observed for these compounds at room temperature.

3.3. Xanthyletin and seselin

The two pyronochromenes showed photochromism on irradiation at 77 K in an EPA matrix [3]. We observed photocoloration after 355 nm laser flash irradiation (11 ns; about 2 mJ pulse) of xanthyletin (8) and seselin (9)



in nitrogen-degassed ethanol at room temperature. The transient absorption spectra obtained by laser flash photolysis at 355 nm of 8 in ethanol and in hexane are shown in Figs. 3 and 4.

The colored form of 8 showed a very intense absorption band at 380 nm and a broad band from 450 to 680 nm with a lower intensity. The rise time monitored at 380 and 590 nm was about 800 ns. The region from 450 to 540 nm was an isosbestic region. On a longer time scale, we found that the bands at 380, 510 and 590 nm were decaying in the microsecond time range. Oxygen caused significant quenching of the entire spectrum. The intensity of the Δ OD spectrum was decreased about tenfold and all rise times were then less than the detection limit (400 ns). The shape of the Δ OD spectrum and the maxima obtained in the oxygen experiment were identical with what was obtained in the nitrogen experiment. The absorption spectrum after time evolution was identical with that obtained in the earlier experiment at 77 K

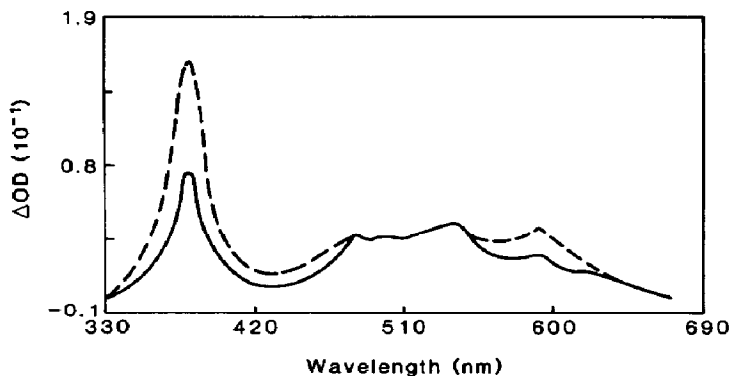


Fig. 3. Transient absorption spectrum (ΔOD spectrum) of **8** in ethanol recorded $1 \mu s$ (—) and $13 \mu s$ (---) after a 355 nm laser flash.

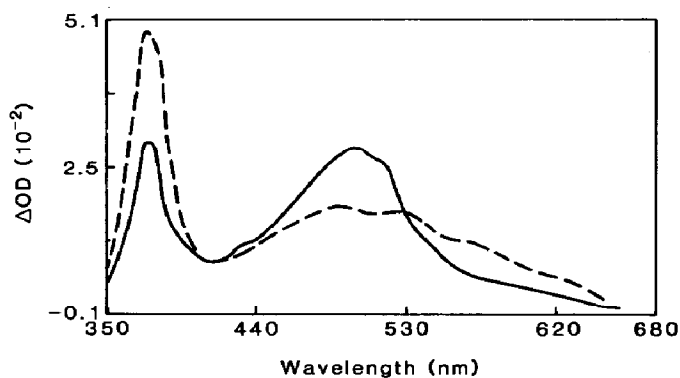


Fig. 4. Transient absorption spectrum (ΔOD spectrum) of **8** in hexane recorded $1 \mu s$ (—) and $13 \mu s$ (---) after a 355 nm laser flash.

in EPA. In view of the results described above, we believe that there is only one colored form with two main absorption bands with maxima at 380 and about 590 nm. This colored form is assigned as the opened quinoid form as before [3].

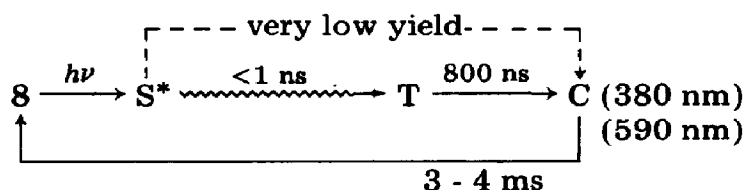
On the basis of the very large quenching by oxygen noted above, the colored form must dominantly arise from the triplet excited state in about 800 ns after excitation of the singlet excited state. The colored form does appear to have a very small origin from an excited singlet state, on the basis of the lack of total quenching in the presence of oxygen. We did not observe any distinctive spectrum characteristic of triplet-triplet absorption but the isosbestic region at about 500 nm gave a very good indication that the triplet state spectrum and the colored form spectrum were highly overlapping. The decay of the triplet-triplet spectrum and the rise of the spectrum of the colored species apparently counteract, giving an isosbestic region.

We also performed identical experiments with **8** in hexane and found a behavior very similar to that given above. We observed the formation of a colored form with an intense absorption band at 370 nm and a broad band between about 450 and about 670 nm. Kinetics studies at 370 and 560 nm gave a rise time of $1.1 \mu s$, whereas a kinetics study at 500 nm gave a decay of

1.1 μs (to a net positive ΔOD resulting from the colored form). The spectrum was also significantly quenched by oxygen (its quenched intensity was approximately threefold less than the corresponding quenched spectrum in ethanol). To verify the existence of a triplet transient further, we also performed an energy transfer experiment with β -carotene by adding it to an ethanol solution of 8 (mole ratio of 8 to β -carotene, 10:1). Excitation of 8 resulted in the formation of the triplet state of β -carotene (maximum absorption at 520 nm) in 600 ns which decayed with a lifetime of 6.6 μs . Therefore, in hexane, a triplet transient clearly exists for 8 with triplet-triplet absorption in the 500 nm region, giving further evidence for the photophysical path given above.

An emission experiment performed in EPA at 77 K gave a blue fluorescence in the 360 - 470 nm region and a green phosphorescence ($\tau_p = 0.58$ s) in the 470 - 580 nm region. We determined the fluorescence lifetime of 8 at 430 nm and 295 K using excitation at 300 nm employing a dye laser. We found a fluorescence lifetime in ethanol of about 650 ps (295 K). To determine the very fast fluorescence lifetime of 8 in hexane at 295 K, we used a streak camera system. We found the fluorescence lifetime to be less than our detection limit of 30 ps. In 3-methylpentane at 77 K the fluorescence lifetime was 1.3 ns. Thus, the radiationless deactivation processes, including photochemistry, out of the lowest singlet excited state are more important in a non-polar solvent at 295 K than in a hydrogen-bonding polar solvent. On the basis of the results at 295 and 77 K in the non-polar solvent (3-methylpentane), there may be an activation energy for formation of the colored form or the rate of internal conversion is decreased as the temperature is decreased. The rate constant for intersystem crossing at 295 K can be estimated to be about 2×10^9 in ethanol and about $10^{10} - 10^{11}$ in hexane.

All the results described above can be summarized in the following scheme for the photophysical process of coloration of 8 in ethanol:



where C is the colored form.

9 irradiated in ethanol in the same manner as previously described for 8 gave a photoproduct with three main bands of absorption at 370, 500 and 580 nm which are very similar to those observed in a steady state experiment at 77 K in EPA [3].

All three bands arose in about 900 ns and decayed in the microsecond time scale. There was no isosbestic region in the visible portion of the spectrum as in the case of 8. However, we did find an absorption band at 310 nm which decayed with a lifetime of 900 ns. When bubbling through oxygen, the

band at 310 nm was totally quenched and the entire spectrum due to the colored form was partially quenched although the amount of quenching of the colored form was approximately three times less than for **8** (also in ethanol). We therefore assign the species at 310 nm to a triplet-triplet absorption band. The large blue shift of this band compared with **8** indicates that the transition is from the lowest triplet state to an excited triplet state T_n where $n > 2$. Also, the contribution of the excited singlet state path to the origin of the colored form is apparently greater than for **8**. The general photo-physical-photochemical path for formation of the colored form of **9** is, however, parallel to that of **8** given above.

We determined the fluorescence lifetime of four different chromenes in various solvents at 295 and 77 K. The results are given in Table 2. For three of the chromenes, we obtained two first-order curves for the decay time of fluorescence. However, the longest first-order component in two cases contributed less than 2% of the total fluorescence signal. We therefore assign this component to a small amount of impurities, or more likely, to delayed scattered light coming from the silver-coated sides of the Dewar.

The fluorescence lifetime of **4** was determined in 2-methyltetrahydrofuran at 295 K and 77 K. The lifetimes were respectively 680 ps and 1.1 ns with monitoring at 360 nm. The difference obtained for the lifetimes can be interpreted as arising from a decrease in internal conversion at 77 K or the existence of an activation energy for formation of the colored form. The benzochromene **7** showed a very weak emission at room temperature and was studied in 2-methyltetrahydrofuran at 77 K using a 400 nm cut-off filter for the monitoring light. We observed two lifetimes contributing equally to

TABLE 2
Fluorescence lifetimes

<i>Compound</i>	<i>Solvent</i>	<i>Temperature</i> (K)	<i>Lifetime τ</i>
4	2-Methyltetrahydrofuran	295	680 ps
		77	1.1 ns 4.6 ns ^a
7	2-Methyltetrahydrofuran	295	Too weak emission
		77	2.6 ns 7.8 ns
8	Ethanol	295	680 ps
	Hexane	295	<30 ps
	3-Methylpentane	77	1.3 ns 4 ns ^a
9	2-Methyltetrahydrofuran	295	Too weak emission
		77	1.6 ns

^aThe contribution of this second component is less than 2% of the overall signal and is assigned to impurity or delayed scattered light.

the fluorescence signal of 2.6 and 7.8 ns. We know from previous studies [3] that, for the benzochromene 5, no emission was observed for the compound itself but the colored form did show fluorescence. Therefore we assign one of the decay components to benzochromene 7 and the other to its opened quinoid form. We were not able to assign the individual components specifically to compound 7 or to its colored form, but the shorter component is most likely the one that originates from the closed form on the basis of the result for 4 given above. Also, since the benzochromene 7 emits only very weakly at room temperature, we assume that the formation of the colored form must have an activation energy. Therefore, the fluorescence would not be expected to be as quenched at 77 K as at room temperature where, for 295 K, the photochemistry could better compete with the emission process. It is also possible that a significant decrease in the internal conversion may also explain this large discrepancy of emission intensity at room temperature compared with 77 K. In both cases, 4 and 7, in view of the short fluorescence lifetime, we assign the fluorescence as arising from a $\pi-\pi^*$ singlet state.

The emission properties of 9 were previously studied in EPA at 77 K [3]. 9 showed a blue fluorescence in the 360 - 470 nm region but no phosphorescence was observed. First, we have to note that, although the triplet state of 9 is occupied on the basis of our results here, phosphorescence was not seen [3]. The fluorescence emission of 9 at 295 K in 2-methyltetrahydrofuran (polar) was too weak to give reliable data. At 77 K, we observed a lifetime of fluorescence of 1.6 ns similar to what we observed in 8 in 3-methylpentane. Again, it is clear that the radiationless processes from the lowest singlet excited state, including photochemistry, are reduced at low temperature compared with room temperature (as also seen for 8). For 8, it is apparent that the hydrogen-bonding solvents have a definite effect on the emission processes, enhancing emission over radiationless paths. The spectra of the photoproducts seem to be independent of the solvent.

In agreement with what we previously reported [3, 4], we assign the emitting state and the photochemically active state to be a singlet $\pi-\pi^*$ state and/or triplet $\pi-\pi^*$ state, depending on the chromene.

Acknowledgments

The laser flash experiments were performed at the Center for Fast Kinetics Research at the University of Texas at Austin, which is supported by National Institutes of Health Grant RR-00886, the Biotechnology Branch of the Division of Research Resources and the University of Texas.

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