

TEMPERATURE DEPENDENCE OF THE PHOSPHORESCENCE LIFETIME OF NITROBENZOPYRANS: THE ROLE OF THE LOWEST TRIPLET STATE IN THE REACTION OF PYRAN RING OPENING

SANDRA MONTI

Istituto di Fotochimica e Radiazioni d'Alta Energia del Consiglio Nazionale delle Ricerche, Bologna (Italy)

GIORGIO ORLANDI

Istituto Chimico "G. Ciamician", Università di Bologna (Italy)

ARLETTE KELLMANN and FRANCIS TFIBEL

Laboratoire de Photophysique Moléculaire, Centre National de la Recherche Scientifique, Orsay (France)

(Received July 23, 1985)

Summary

The temperature dependence of the phosphorescence lifetime of 6-nitro-8-methoxy-2,2,3-trimethyl-2*H*-chromene and of spiro[8-methoxy-6-nitro-2*H*(1)-benzopyran-2,2'-3',3'-dimethylpiperidine] and its 3-methyl-substituted derivative has been investigated in an alkane mixture in the range 77 - 160 K. It has been found that the main non-radiative deactivation channel for the T_1 state is a spin-allowed process with an activation barrier of about 5 kcal mol⁻¹. A fairly good agreement with previous laser photolysis studies is found. It is concluded that the activated process competing with emission at low temperatures is the rupture of the C—O bond in the pyran ring.

1. Introduction

Benzopyran derivatives are known for their photochromic properties. The structural changes associated with this phenomenon are the photo-induced cleavage of the C—O bond in the pyran ring and the isomerization to open coloured isomers with quinoid structure [1]. The photoisomerization reaction mechanism has been widely studied for the nitro-spiro-benzopyran class of compounds, mainly the indolino series, and the prominent role of triplet states has been demonstrated by sensitization [2 - 4], pressure effects [5] and pulsed photolysis techniques [6 - 8]. However, in the literature, different hypotheses have been formulated about the mechanism of the triplet photoreactivity. A study of the ability of triplet energy donors to

sensitize photoisomerization and/or phosphorescence in a poly(methyl methacrylate) matrix, showed that a higher triplet and not the phosphorescent state is photoreactive [3]. On the basis of picosecond laser photolysis, an upper vibrational level of the lowest triplet state has been proposed as being responsible for the photoreaction [9]. Results from other studies have indicated that the vibrationally relaxed lowest triplet is the reactive state for colour formation either via unimolecular [2, 4, 6, 7] or bimolecular processes [8].

Recent studies by nanosecond laser photolysis on the primary events in the photochromism of the nitro-substituted benzopyran derivatives illustrated in Fig. 1 have shown that, in solution, photoinduced opening of the pyran ring occurs adiabatically on the lowest triplet energy surface through an activated process [10 - 12]. This conclusion was based on the observation of a transient absorption showing a thermally activated decay rate constant with a pre-exponential factor of about 10^{12} s^{-1} which was attributed to the $T_n \leftarrow T_1$ absorption.

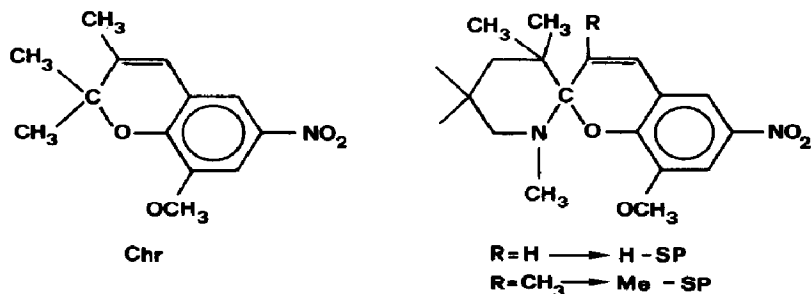


Fig. 1. Structure of the nitro-substituted benzopyran derivatives under study.

To confirm this assignment, we have now investigated the kinetic parameters of the $T_1 \longrightarrow S_0$ phosphorescence of the nitrobenzopyrans in a range of temperatures from 77 to 160 K. At these temperatures the presence of an activated process competing with emission can be easily observed and its parameters determined.

2. Experimental details

The chromene 6-nitro-8-methoxy-2,2,3-trimethyl-2*H*-chromene (Chr) and the spiropyran spiro[8-methoxy-6-nitro-2*H*(1)-benzopyran-2,2'-3',3'-dimethylpiperidine] (H-SP) and its 3-methyl-substituted derivative (Me-SP) were synthesized according to ref. 13 and ref. 14 respectively. The solvents 3-methylpentane (3MP) and methylcyclohexane (MeCH) (Carlo Erba) were passed twice through a 50 cm column of freshly activated silica gel and the purity was fluorometrically controlled. 50vol.%3MP-50vol.%MeCH was used as the solvent. Concentrations were chosen such that the absorbances were about 0.4 at 337 nm for a path length of 10 mm (about $5 \times 10^{-5} \text{ M}$). All

samples were sealed under vacuum after repeated freeze-pump-thaw cycles in 10 mm quartz cells or in capillary tubes.

Low temperatures (90 - 160 K) were maintained with a Thor C600 nitrogen-flow cryostat, equipped with a Thor 3030 temperature controller and indicator. The absolute error is estimated to be ± 2 K. Measurements at 77 K were carried out in capillary tubes immersed in liquid nitrogen.

Emission spectra were measured using a Perkin-Elmer MPF-44B spectrofluorometer equipped with a DCSU-2 differential corrected spectra unit (correction for $\lambda \leq 600$ nm). Emission lifetimes were measured by exciting the samples using a pulsed nitrogen laser (Lambda Physik M100A, 3.5 ns full width at half-maximum, $\lambda = 337$ nm, 3 mJ). Emission decays were detected at 493 nm, using a narrow band interference filter (Balzers) by means of Hamamatsu R955 or RCA 1P28 photomultipliers (nine dynodes connected, load 15 k Ω) and a digital storage oscilloscope (Tektronix model 468). The data treatment was carried out with a PDP 11/23 Digital micro-computer. Standard iterative non-linear procedures were employed to analyse the decay curves. Single exponential decays were observed in all cases. The uncertainty in the Arrhenius parameters was ± 0.5 kcal mol $^{-1}$ for E_a and ± 0.4 for log A .

3. Results and discussion

The three benzopyran derivatives studied are known to be phosphorescent [4, 14, 15]. Emission spectra, measured at 77 K in the rigid alkane glass, are shown in Figs. 2(a), 3(a) and 4(a). This emission has been recognized to be typical of a $^3\pi\pi^*$ state localized on the nitrochromene part of the molecule with partial intramolecular charge transfer character [4, 14 - 16]. Triplet decay rate constants k_0 at 77 K (Table 1) are typical of nitroaromatic molecules [17] and are in agreement with previous determinations [4, 14, 15].

The temperature dependence of the phosphorescence decay rate parameter, observed in the range 77 - 160 K, is shown in Figs. 2(b), 3(b) and 4(b). In the case of Chr, some permanent photodegradation occurs [10]; therefore to obtain the plot of Fig. 2(b) samples were irradiated with a few laser shots and were frequently renewed.

TABLE 1

Kinetic parameters for the phosphorescence decay of nitrobenzopyran derivatives in 50vol.%3MP-50vol.%MeCH

	k_0 (s $^{-1}$)	A (s $^{-1}$)	E_a (kcal mol $^{-1}$)
Chr	4.5	2.2×10^{11}	5.0
H-SP	3.8	2.1×10^{12}	4.6
Me-SP	5.2	3.5×10^{12}	5.2

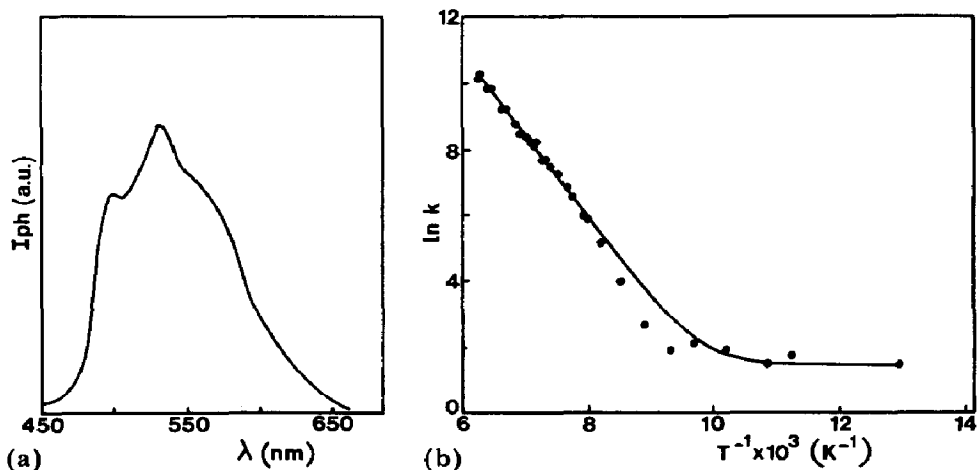


Fig. 2. (a) Corrected phosphorescence spectrum of Chr in 50vol.%3MP-50vol.%MeCH at 77 K and (b) plot of $\ln k$ vs. $1/T$; $\lambda_{\text{exc}} = 337$ nm.

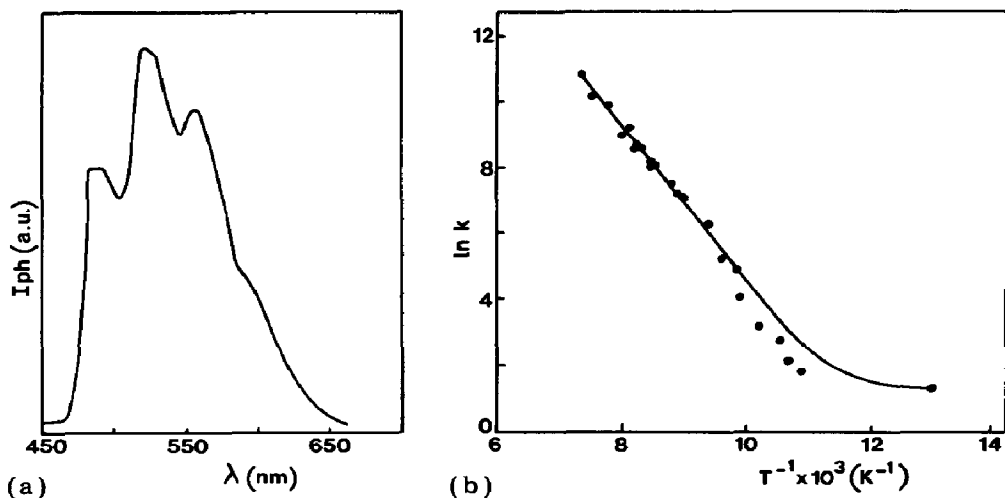


Fig. 3. (a) Corrected phosphorescence spectrum of H-SP in 50vol.%3MP-50vol.%MeCH at 77 K and (b) plot of $\ln k$ vs. $1/T$; $\lambda_{\text{exc}} = 337$ nm.

In the case of the two spiropyrans, no appreciable permanent photo-degradation was observed; the reported plots are the results of at least three independent experiments. For Chr and H-SP, the formation of a metastable open isomer occurs with high yield [10, 11]. This prevents the quantitative correlation of emission intensities with decay rate constants. Such a correlation was found only for Me-SP (see Fig. 4(b)), owing to the lower photoisomerization yield [12].

The $\ln k$ versus $1/T$ plots are linear above 110 - 120 K. The continuous lines correspond to the best fit of the experimental points to the equation

$$k = k_0 + A \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

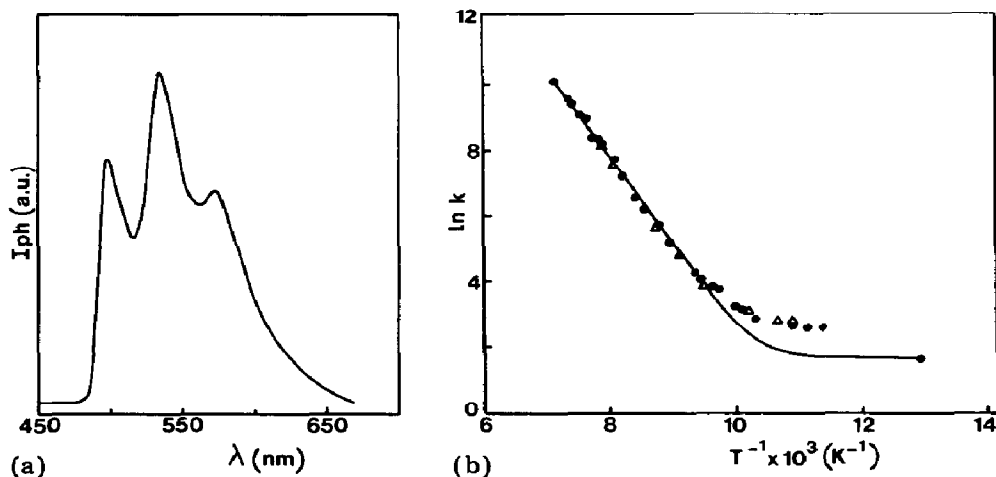


Fig. 4. (a) Corrected phosphorescence spectrum of Me-SP in 50vol.%3MP-50vol.%MeCH at 77 K and (b) plot of $\ln k$ vs. $1/T$; $\lambda_{\text{exc}} = 337$ nm. (Δ , $\ln 1/\phi_{\text{rel}}$ (ϕ_{rel} , relative emission intensity).)

where the constant term k_0 has been assumed to be equal to the decay rate parameter measured at 77 K. The agreement between the experimental data and the calculated curve is good above 110 - 120 K, and the extracted Arrhenius parameters are reported in Table 1. Strong deviations occur between 77 and 110 - 120 K. In this range other temperature-dependent processes, not represented by eqn. (1), seem to take place. In particular, a rigid-fluid transformation of the matrix takes place with strong changes in viscosity. This can markedly affect the kinetic properties of the triplet state. In fact, viscosity is expected to influence triplet lifetimes especially for molecules with low frequency modes with a large amplitude which involve the motion of sizable groups [18]. Above 120 K the solvent is fluid and the triplet decay kinetics is determined essentially by intramolecular properties while effects due to the medium become of minor importance. This interpretation has been confirmed by a parallel study performed on a completely different molecular system in the same solvent. (The temperature dependence of the phosphorescence lifetime of benzophenone in the same solvent and in the same temperature range was determined. This molecule was chosen as the triplet lifetimes are of the same order as those of nitrobenzopyrans above 120 K. Equation (1) satisfactorily describes the experimental data over the whole temperature range and the derived kinetic parameters are $k_0 = 1.6 \times 10^2 \text{ s}^{-1}$, $E_a = 3.0 \text{ kcal mol}^{-1}$ and $A = 8.3 \times 10^8 \text{ s}^{-1}$. These values are completely different from those exhibited by benzopyrans and are in good agreement with the reported temperature dependence of the intermolecular hydrogen-abstraction rate parameter [19].)

The pre-exponential factors A (Table 1) are of the order of the molecular vibration frequencies and of the pre-exponential factors A' of diffusion rate constants [20]. Triplet quenching by impurities can be ruled out in this

case since the pre-exponential factor for such a process, for a quencher concentration $[Q]$, is $A'[Q]$. Since $[Q] \ll 1$, $A'[Q] \ll A$ [20]. Thus, it is reasonable to conclude that the rate determining process in the decay of the closed form triplet (T_1) is an intramolecular deactivation transition.

The values of the activation energies and the pre-exponential factors determined in the present work are in agreement with those of previous studies, in which the triplet state was observed at room temperature by nanosecond laser photolysis [10 - 12]. The temperature dependence of the $T_n \leftarrow T_1$ absorption decay rate parameter, observed in toluene in the range 273 - 323 K, was found to be consistent with an activated process characterized by energy barriers of about 8 kcal mol⁻¹ and 5.5 kcal mol⁻¹ and pre-exponential factors of about 5×10^{12} s⁻¹ and 1×10^{11} s⁻¹ for Chr [10] and Me-SP [12] respectively. A secondary triplet decay channel with negligible activation energy (about 0.5 kcal mol⁻¹) and a lower pre-exponential factor ($10^6 - 10^7$ s⁻¹), assumed to be $T_1 \rightarrow S_0$ intersystem crossing (ISC), was postulated to explain both the spectral features of the intermediates [10, 12] and the temperature dependence of the quantum yield of the photoisomerization [10]. There is fairly good agreement between the Arrhenius parameters of the T_1 decay determined by $T_n \leftarrow T_1$ absorption near room temperature [10 - 12] and phosphorescence at low temperatures; however, in the present study, no evidence has been found for the assumed $T_1 \rightarrow S_0$ ISC process.

The determined activation barriers of about 1700 cm⁻¹ are much lower than the energy gap between T_1 and the next higher triplet T_2 , which was computed to be about 3500 cm⁻¹ [16]. It is therefore suggested that the T_1 decay is associated with an adiabatic motion over a barrier leading to a triplet T_x which is another minimum on the same potential energy surface as that of T_1 .

According to theoretical calculations, the coordinate along which the molecule moves is that of a torsion in the pyran ring coupled to the C—O bond cleavage [16]. The initial step in this motion is the same for the three compounds and it is probably common to all *p*-nitro-substituted benzopyran derivatives. The subsequent evolution of the molecule from the T_x geometry is, on the contrary, strongly dependent on the specific molecular structure: Chr and H-SP continue the motion along the reaction coordinate to other minima in the T_1 energy surface from which they decay to the ground state of the open form; Me-SP, owing to the steric hindrance introduced by the methyl groups in the 3-position and the 3'-position, decays from the T_x geometry back to the ground state of the closed form [12].

Acknowledgments

We wish to thank Dr. L. Lindqvist of the Laboratoire de Photophysique Moléculaire, Centre National de la Recherche Scientifique, Orsay, for helpful discussions concerning this paper, and we are indebted to Professor R. Guglielmetti of the Université d'Aix-Marseille II for having raised our interest

in this field and for the synthesis of the compounds. We also thank Dr. F. Barigelletti of the Istituto di Fotochimica e Radiazioni d'Alta Energia for useful discussions about the data treatment. Mr. L. Minghetti and Mr. L. Ventura are also acknowledged for technical assistance.

References

- 1 R. C. Bertelson, in G. H. Brown (ed.), *Photochromism*, Wiley-Interscience, New York, 1971, Chapter 3.
- 2 G. I. Lashkov, V. L. Ermolaev and A. V. Shablya, *Opt. Spektrosk.*, 21 (1965) 305.
H. Bach and J. Calvert, *J. Am. Chem. Soc.*, 92 (1970) 2608.
- 3 D. A. Reeves and F. Wilkinson, *J. Chem. Soc., Faraday Trans. II*, 9 (1973) 1381.
- 4 P. Appriou, R. Guglielmetti and F. Garnier, *J. Photochem.*, 8 (1978) 145.
- 5 D. G. Wilson and H. G. Drickamer, *J. Chem. Phys.*, 63 (1975) 3649.
- 6 T. Bercovici, R. Heiligman-Rim and E. Fischer, *Mol. Photochem.*, 1 (1969) 23, and references cited therein.
- 7 Yu. P. Strokach, V. F. Mandzhikov, V. A. Barachevskii, N. D. Dimitreva and R. M. Liberzon, *Opt. Spektrosk.*, 47 (1979) 997; 49 (1980) 1195.
V. A. Murin, V. F. Mandzhikov and V. A. Barachevskii, *Opt. Spektrosk.*, 40 (1976) 1084.
- 8 V. Krongauz, J. Kiwi and M. Grätzel, *J. Photochem.*, 13 (1980) 89.
Y. Kalisky, T. E. Orłowski and D. J. Williams, *J. Phys. Chem.*, 87 (1983) 5333.
- 9 S. A. Krysanov and M. V. Alfimov, *Chem. Phys. Lett.*, 86 (1982) 100.
Dokl. Akad. Nauk SSSR, 272 (1983) 406.
- 10 S. Monti, A. Kellmann, F. Tfibel and R. Guglielmetti, *J. Photochem.*, 17 (1981) 76.
A. Kellmann, L. Lindqvist, S. Monti, F. Tfibel and R. Guglielmetti, *J. Photochem.*, 21 (1983) 223.
- 11 A. Kellmann, F. Tfibel, L. Lindqvist, S. Monti and R. Guglielmetti, *Proc. Xth IUPAC Symp. on Photochemistry, Interlaken, July 22 - 27, 1984*, Presses Polytechniques Romandes, Lausanne, 1984, p. 373.
- 12 A. Kellmann, L. Lindqvist, S. Monti, F. Tfibel and R. Guglielmetti, *J. Photochem.*, 28 (1985) 547.
- 13 E. Davin-Pretelli, M. Giuliano, G. Mille, J. Chouteau, R. Guglielmetti and C. Gelebart, *Helv. Chim. Acta*, 60 (1977) 215.
- 14 G. Petillon, *Doctoral Dissertation*, Laboratoire de Synthèse Organique, Université de Bretagne Occidentale, Brest, 1979.
- 15 P. Appriou, R. Guglielmetti, A. Botrel and A. Le Beuze, *J. Photochem.*, 8 (1978) 73.
- 16 F. Zerbetto, S. Monti and G. Orlandi, *J. Chem. Soc., Faraday Trans. II*, 80 (1984) 1513.
- 17 O. S. Khalil, H. G. Bach and S. P. McGlynn, *J. Mol. Spectrosc.*, 35 (1970) 455.
- 18 W. G. Herkstroeter and D. S. McClure, *J. Am. Chem. Soc.*, 90 (1968) 4522.
- 19 N. J. Turro, *Modern Molecular Photochemistry*, Benjamin-Cummings, Menlo Park, CA, 1978, pp. 235 - 238.
- 20 R. Livingston and W. Ware, *J. Chem. Phys.*, 39 (1963) 2593.
A. H. Alwattar, M. D. Lumb and J. B. Birks, in J. B. Birks (ed.), *Organic Molecular Photophysics*, Wiley, New York, 1973, Chapter 8.