The Relaxation of Electronically Excited Styrenes: a ' Twisted ' Excited State

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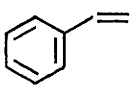
Gas-phase studies of a series of styrene derivatives have provided evidence for relaxation from initially excited ^1L_a states to ' twisted ' singlet states which have anomalously long lifetimes. By examining derivatives with different constraints for rotation about the excited π-bond it has been demonstrated that it is a change in excited state geometry involving some rotation which controls the efficiency of population of the long-lived singlet states. Comments on a recent analysis of the solution phase photophysics of cyclic styrene derivatives are made.

As part of our studies of the photochemistry and photophysics of styrenes [1,2] we recently reported the application of time resolved spectroscopy to the problem of analysing the relaxation routes of electronically excited styrenes.[3] We noted that excitation of styrene (1), *trans*-1-phenylpropene (2), and 1-phenylcyclobutene (3) in their ^1L_a bands resulted in dual emissions. (Here we are assuming the simplest analysis. In fact there may be more than two excited states responsible for the total emission.) One component emitting on the blue side of the total fluorescence spectra has a long lifetime in each case and the other component emitting on the red side of the total fluorescence spectra has a short lifetime. We suggested that the red shifted emission (relative to the fluorescence spectrum resulting from 0–0 excitation in the ^1L_b band) is due to emission from high vibrational levels of the ^1L_b state. The red shift is the result of the Franck–Condon factors which couple high vibrational levels of the ^1L_b state with high vibrational levels of the ground state.



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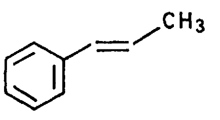

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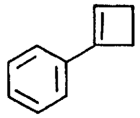

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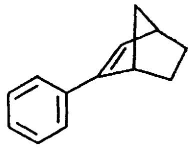

(4)

We suggested the long-lived blue shifted components might be the result of molecular distortions, possibly rotation about the essential double bond, leading to the population of ' twisted ' states with their own characteristic radiative and non-radiative rate constants.

We now report some results which provide strong evidence that rotation about the excited π-bond is indeed involved in the production of the anomalous long-lived fluorescent states.

EXPERIMENTAL

Materials.—Styrene was purchased from Koch–Light Ltd. All the styrene derivatives were synthesised by literature methods involving the addition of a Grignard reagent or phenyl-lithium to an aldehyde or ketone followed by dehydration of the alcohol. Toluene-*p*-sulphonic acid was found to be the dehydration catalyst giving the most consistently high yields of products. All the styrenes were purified by preparative g.l.c. (immediately before use) on a 20% QF 1 on diatomite C column.

Time Resolved Spectroscopy and Fluorescence Wavelength Resolved Lifetimes.—The apparatus which employs a frequency doubled Ar^+ laser has been described elsewhere.[4] The time gate employed was *ca.* 2 ns and the spectral resolution was 5 Å.

Single Photon Counting Apparatus (used to obtain τ_F *on Excitation in the* ^1L_b *Band).*—This apparatus, which was constructed by incorporating the desirable features of a number of systems in the literature has recently been described.[5]

Static Excitation and Fluorescence Spectra Measurement.—The spectrofluorimeter used was one which employed front surface observation and a deuterium lamp (Hanau; D 200 F). A high intensity Bausch and Lomb monochromator and a D 330/D 331 double grating monochromator were used as the excitation and emission monochromators respectively. Light detection was by means of a cooled (0 °C) E.M.I. 6256 QB photomultiplier tube operated at 1300 V. The photomultiplier output was fed to a Brookdeal 5 Cl single photon counter *via* a fast pre-amplifier (Ortec 9301). After being counted and stored, the accumulated counts were converted to a direct current signal and displayed on a chart recorder.

RESULTS

Figure 1 shows the gas-phase absorption spectrum of styrene (1) and Figure 2a the fluorescence decay curves

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[1] M. G. Rockley and K. Salisbury, *J.C.S. Perkin II*, 1973, 1582.

[2] K. Salisbury, *J. Photochem.*, 1974, **2**, 40; P. M. Crosby and K. Salisbury, *J.C.S. Chem. Comm.*, 1975, 477.

[3] R. P. Steer, M. D. Swords, P. M. Crosby, D. Phillips, and K. Salisbury, *Chem. Phys. Letters*, 1976, **43**, 461.

[4] M. D. Swords and D. Phillips, *Chem. Phys. Letters*, 1976, **43**, 228.

[5] R. Brentnall, P. M. Crosby, and K. Salisbury, *J.C.S. Perkin II*, 1977, 2022.

produced on excitation of styrene (0.1 mmHg) by a frequency doubled argon ion 2 W laser (257.25 nm). It can be seen that the long wavelength component has a relatively short lifetime (τ short) and the fluorescence lifetimes increase with decreasing emission wavelength. The two component nature of the total fluorescence is also demonstrated by Figure 2b where the late gated spectrum (t + 35 ns) is considerably blue-shifted in comparison with the early spectrum. This situation is also clearly reproduced by the static fluorescence spectrum of styrene measured at different excitation wavelengths (Figure 3). Thus on excitation of styrene (1.0 mmHg) at 287 nm (near the 0–0 band for excitation to the ^1L_b state), the familiar fluorescence spectrum of relaxed styrene is produced. Moving to shorter excitation wavelengths a broadening of the emission spectrum is seen and on excitation at 257.0 nm distinct red- and blue-shifted tails are present. Figure 4 shows the effect of vibrational quencher on the emission spectrum produced by 257.0 nm excitation.

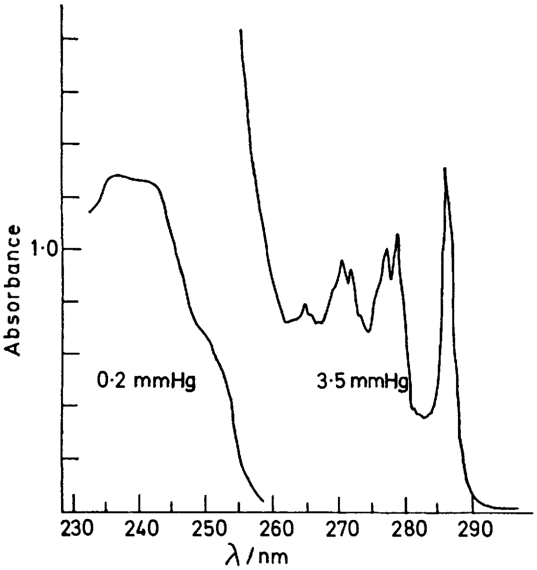

FIGURE 1 The absorption spectrum of styrene measured at 0.2 mmHg up to 260 nm and at 3.5 mmHg from 255 to 295 nm. Cell path length 10 cm

TABLE 1

Fluorescence lifetimes of the short- and long-lived emitting states following excitation at 257.25 nm. Sample pressure 0.10 mmHg

	τ_F(Short)/ns [a]	τ_F(Long)/ns [b]
Styrene	1.5	50.0
trans-1-Phenylpropene	2.0	45.0
1-Phenylcyclobutene	3.0	70.0
2-Phenylnorborn-2-ene	4.5	

[a] Lifetimes given to nearest 0.5 ns and measured at emission wavelength 330 nm. [b] Lifetimes given to nearest 0.5 ns and measured at emission wavelength 280 nm.

Similar observation of the fluorescence wavelength resolved lifetimes and time resolved fluorescence spectra were obtained for *trans*-1-phenylpropene. Table 1 gives the lifetimes of the long-lived components (measured at emission wavelength 280 nm) and the short-lived components (measured at 330 nm).

1-Phenylcyclobutene (3) was also examined in order to obtain information concerning the importance of rotation about the olefinic double bond in populating the long-lived states. The initially surprising results are shown in Table 1 and the time resolved spectra were qualitatively similar to those of styrene. 2-Phenylnorborn-2-ene (4) was chosen as a model compound in which rotation about the double bond in the excited states should be inhibited by the bicyclic ring constraints. Unlike the other systems so far studied, 2-phenylnorborn-2-ene shows no change in the total fluorescence spectrum (only a decrease in ϕ_F) on going from 280 to 257 nm excitation (Figure 5). Furthermore, as Figure 6 shows, the fluorescence lifetimes are independent of the emission wavelength at which they are measured.

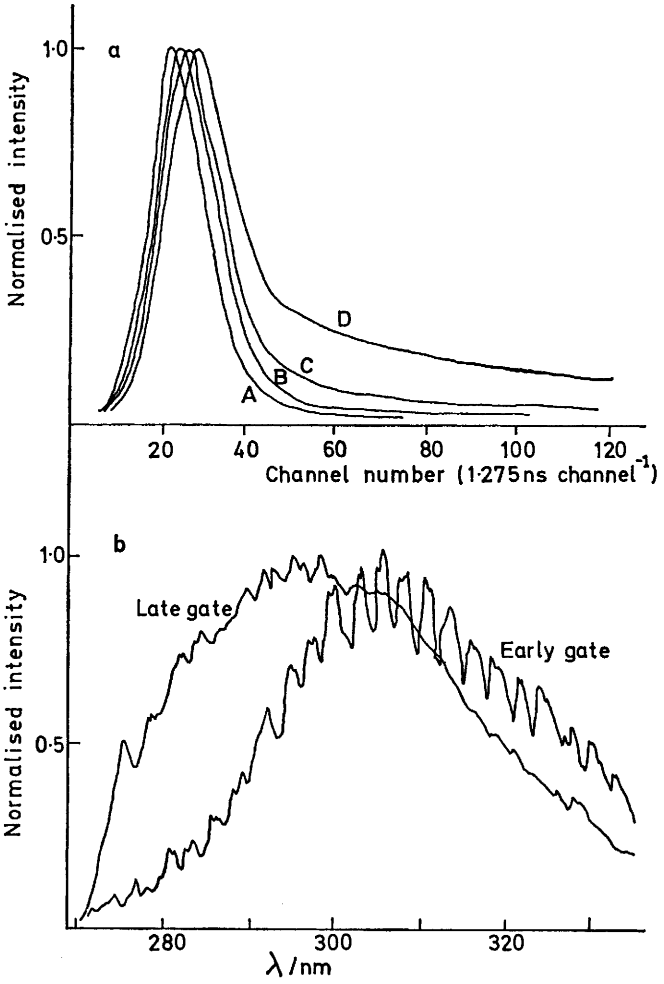

FIGURE 2 a, Decay profiles of fluorescence from styrenes as a function of emission wavelength (pressure 0.1 mmHg): A, λ 257.25 nm, pump pulse; B, λ 330 nm; C, λ 290 nm; D, λ 280 nm. b, Gated fluorescence spectra of styrene; laser excitation at 257.25 nm. The early gated spectrum represents the emission occurring during the laser excitation pulse. The late gated spectrum is taken 35 ns later

Table 2 gives the available fluorescence lifetimes of some styrene derivatives on excitation to the zeroth vibrational level of the ^1L_b band.

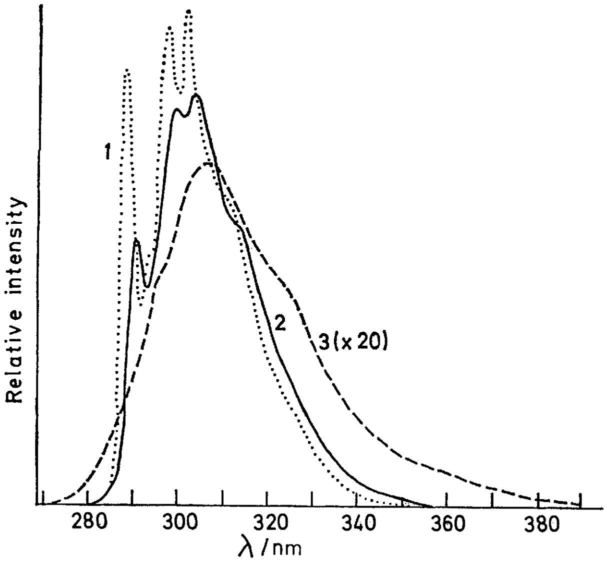

FIGURE 3 Fluorescence spectra of styrene (1.0 mmHg) for different excitation wavelengths: 1, 287 nm; 2, 282 nm; 3, 257 nm

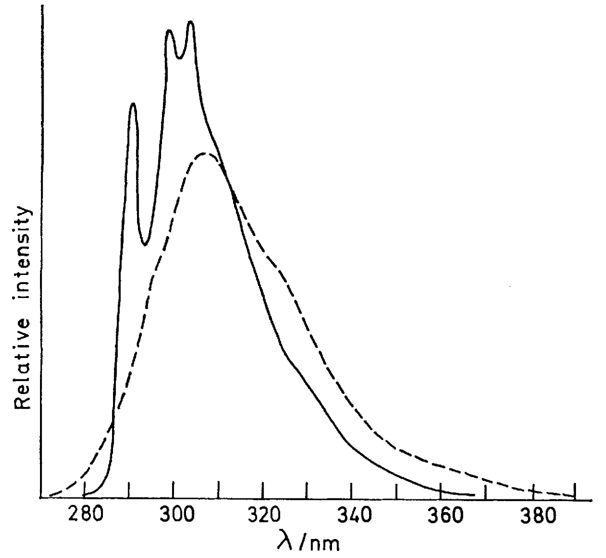

FIGURE 4 Fluorescence spectra of styrene (1.0 mmHg) excited at 257 nm, with (——) and without (– – – –) 700 mmHg of butane

TABLE 2

Fluorescence lifetimes following excitation at 285.0 nm. Sample pressures between 0.1 and 1.0 mmHg

	τ_F/ns (single exponential)	$10^{-7}k_{NR}/s^{-1}$
Styrene	20.8 (20.3) [a]	3.2
trans-1-Phenylpropene	18.0	4.8 [b]
1-Phenylcyclobutene	20.0	3.3 [c]
1-Phenylcyclohexene	17.4	3.7
(*E*)-2-Phenylbut-2-ene	17.0	

[a] Taken from ref. 6. [b] Taken from ref. 1. [c] Calculated assuming Zimmerman's values for k_R.[7]

DISCUSSION

This extension of our earlier work on the decay processes resulting from excitation into the ^1L_a band of styrenes confirms that in the case of acyclic styrenes excitation leads to two component emissions. The early and late gated spectra of styrene show a shift of 12 nm with the early spectum exhibiting considerable structure (Figure 2b). The changes in the total fluorescence spectra on changing the excitation wavelength from 287.0 nm (population of the vibrationless and first few vibrational levels of the ^1L_b state) to excitation in the ^1L_a band (257.0 nm) are clearly shown in Figure 3. The growth in both long and short wavelength tails supports the spectral observations made using the time resolved technique. Taking the value of Hui and Rice [6] for ϕ_F on excitation at 287 nm as 0.36 we can estimate ϕ_F for 256 nm excitation as 0.01. This is composed of ϕ_F

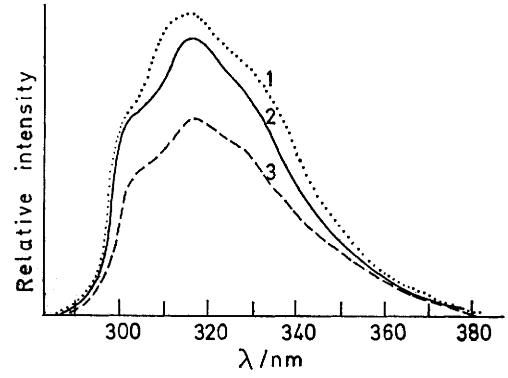

FIGURE 5 Fluorescence spectra of 2-phenylnorborn-2-ene (0.03 mmHg) for different excitation wavelengths: 1, 280 nm; 2, 270 nm; 3, 257 nm

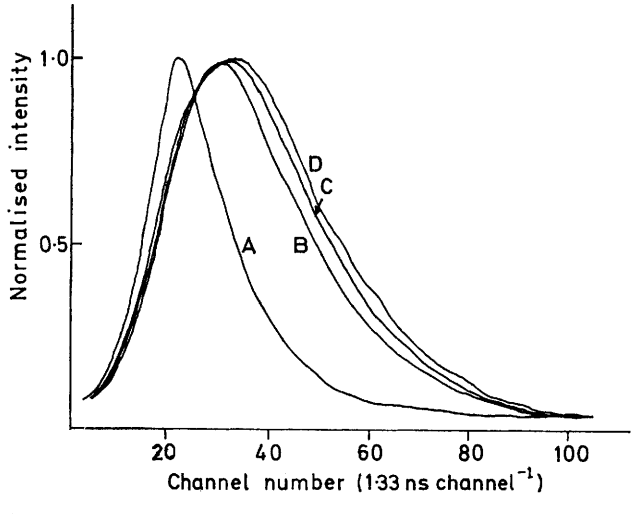

FIGURE 6 Decay profiles of fluorescence from 2-phenylnorborn-2-ene as a function of emission wavelength (pressure 0.10 mmHg): A, λ 257.25 nm, pump pulse; B, λ 280 nm; C, λ 305 nm; D, λ 330 nm

[6] M. H. Hui and S. A. Rice, *J. Chem. Phys.*, 1974, **61**, 833 and references cited therein.

(short) and ϕ_F (long). However, since the two emissions are strongly overlapping it is very difficult to determine the individual contributions at this stage. We can do no better than estimate that ϕ_F (long): ϕ_F (short) is *ca.* 1 : 10. Therefore, taking into account that geometric isomerisation of *trans*-1-phenylpropene is only of minor importance on excitation into the ^1L_a band (λ_{ex} 250 nm; $\phi_{t \longrightarrow c} < 0.05$), we must conclude that other non-radiative processes including dissociation are of importance. Figure 4 shows that vibrational relaxation and collision induced internal conversion occurs when styrene and a high pressure of inert relaxer is excited at 257.0 nm so that under these conditions the fluorescence spectrum is very similar to that produced on excitation of 1.0 mmHg at 287.0 nm.

Having established the general behaviour of the two acyclic styrenes, styrene and *trans*-1-phenylpropene on excitation in their ^1L_a bands, we wished to investigate the importance of the freedom of rotation about the essential double bond (olefinic double bond) in the ^1L_a state in populating the long and short-lived emitting states. We therefore investigated 1-phenylcyclobutene hoping that the constraint imposed by the small ring would prevent any large changes in geometry in the excited state. However, time resolved spectroscopy and an analysis of the dependence of τ_F on emission wavelength gave qualitatively similar results to those obtained for styrene and *trans*-1-phenylpropene. One significant difference was the very long lifetime (70 ns) of the blue-shifted component in the case of phenylcyclobutene (see Table 1).

We therefore suggest that the molecular distortion necessary to produce the long-lived states in styrenes is relatively small. In the case of phenylcyclobutene molecular models indicate that a rotation of *ca.* 10—15° about a bond formed between two sp^2 hybrid orbitals in which no p-π overlap is present (*i.e.* cyclobutene with no p-π overlap approximates to a twisted excited phenylcyclobutene) can occur with little increase in strain energy of the ring. Furthermore, if one of the major non-radiative relaxation routes of the ' twisted ' long-lived state involves further rotation about the sp^2–sp^2 carbon atoms, it seems reasonable that this would be prevented by ring strain and thus lead to an increased lifetime compared with the acyclic styrenes. 2-Phenylnorborn-2-ene was then chosen for examination since this is a styrene derivative in which little rotation about the olefinic double bond (in the excited state) is possible as a result of the severe constraints imposed by the ring system. This model compound turned out to be a good choice, since as Figures 5 and 6 show, no long-lived component is observed on excitation at 257.0 and 257.25 nm. Thus the early and late gated spectra are superimposable and the fluorescence spectrum is independent of excitation wavelength (although there is a change in ϕ_F). We therefore suggest that the long-lived singlet states produced by excitation into the ^1L_a bands of styrene derivatives are ' twisted ' singlet states, *i.e.* states formed by a change in geometry of the excited state involving, at least in part, a rotation about the olefinic double bond.

The lack of red shift in the short-lived component of phenylnorbornene is almost certainly the result of geometric constraints affecting the $^1L_b \longrightarrow$ ground state emission (we have suggested earlier that the short lived states are high vibrational levels of the ^1L_b electronic states).[3]

Comments on the Effect of Ring Constraints on the Radiationless Decay of the ^1L_b *States of Styrenes.*— Recently Zimmerman and his co-workers[7] presented a set of singlet state non-radiative rate constants (k_{NR}) obtained for 1-phenylcyclo-butene, -pentene, -hexene, and -heptene in solution. It was suggested that the increase in k_{NR} (4.6, 3.3, 67, and 349 × 10^7 s^{-1}, respectively) with increase in ring size demonstrated the overall control of k_{NR} by the ability of the molecules to undergo twisting about the excited π-bond. Since this was a solution study it is reasonable to suppose that in every case fluorescence and non-radiative decay occurred from the equilibrated ^1L_b states. Our initial gas-phase studies indicate that this is an over-simplification and that the environment plays an important part in controlling k_{NR}. Thus as Table 2 demonstrates, in the gas phase the differences between the values of k_{NR} for acyclic styrenes and 1-phenylcyclo-butene and -hexene are small. This may indicate that the amount of rotation about the excited π bond in the ^1L_b state necessary in order to achieve irreversible depopulation of the vertical state (*i.e.* non-radiative decay) is small for the isolated molecule. The constraints imposed by ring strain may be important further along the potential energy surface for rotation but they need not influence the rate of non-radiative depopulation of the vertical emitting state. No speculation as to the way in which solvent interactions may perturb the system will be put forward.

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[7] H. E. Zimmerman, K. S. Kamm, and N. P. Werthman, *J. Amer. Chem. Soc.*, 1975, **97**, 3718.