

The Triplet State of Styrenes

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The energy levels of the S_1 , S_2 , and T_1 states of a range of cyclic and acyclic phenylalkenes have been determined and the structure-excited state energy level relationship examined. The S_2 (Franck-Condon maximum) - T_1 (absorption onset) energy gap is a constant for all the systems studied ($189.5 \pm 4 \text{ kJ mol}^{-1}$), except the severely twisted *cis*-*t*-butylstyrene, and thus allows the determination of the triplet energy of simple phenylalkenes merely by obtaining the S_0 - S_n spectra. An extensive search for phosphorescence (on direct irradiation and triplet sensitisation) even at 10 K in a nitrogen matrix was unsuccessful and this may be interpreted in terms of a non-radiative relaxation requiring little molecular distortion.

In the study of the solution phase photochemistry of any class of molecules, it is essential to establish the energies and characters of the lowest excited singlet and triplet states. In many simple molecules which have well resolved S_0 - S_n absorption spectra and which phosphoresce, acquiring this information is a trivial problem. However, in more complex molecules which have congested, poorly resolved S_0 - S_n absorption spectra and which do not phosphoresce, serious difficulties arise. The styrenes currently being studied by us¹ and others²⁻⁴ are an example of the latter class of molecules. The S_0 - S_1 (1A - 1B) and S_0 - S_2 (1A - 1A) absorption bands are very close in energy and since the S_0 - S_2 transition is strongly allowed while the S_0 - S_1 transition is only weakly allowed much of the structure of the latter transition is lost in the tail of the S_0 - S_2 transition. Furthermore as far as we

know, a styrene has never been observed to phosphoresce.

The aim of the present study was to establish the energy levels of the lower excited states of a series of styrenes and to probe the radiative and non-radiative relaxation routes of the triplet states.

RESULTS

Table 1 shows the λ_{max} values for the S_0 - S_2 transitions [formally (1A_1 - 1A_1)] and the longest wavelength vibrational bands (assigned the 0-0 bands by analogy with styrene^{5,6}) of the S_0 - S_1 transition [formally (1A_1 - 1B_2)] measured for perfluoromethylcyclohexane solutions. The fluorescence spectra of all the styrenes studied have been obtained for perfluoromethylcyclohexane solution and in every case the 0-0 vibrational band for emission from the 1B_2 state is seen at the same wavelength as in absorption.

⁴ H. E. Zimmerman, K. S. Kamm, and D. P. Wertheman, *J. Amer. Chem. Soc.*, 1974, **96**, 7821.

⁵ W. W. Robertson, J. F. Music, and F. A. Matson, *J. Amer. Chem. Soc.*, 1950, **72**, 5620.

⁶ A. Hartford, jun., and J. R. Lombardi, *J. Mol. Spectroscopy*, 1970, **35**, 413.

¹ (a) M. G. Rockley and K. Salisbury, *J.C.S. Perkin II*, 1973, 1582; (b) P. M. Crosby and K. Salisbury, *J.C.S. Chem. Comm.*, 1975, 477.

² M. H. Hui and S. A. Rice, *J. Chem. Phys.*, 1974, **61**, 833.

³ C. S. Nakagawa and P. Sigal, *J. Chem. Phys.*, 1973, **58**, 3529.

The emission spectra of *cis*- and *trans*-1-phenylpropene, *trans*-1-phenyl-3,3-dimethylbut-1-ene, 1-phenylcyclobutene, and 1-phenylcyclopentene were measured at 10 K in nitrogen matrices. The well resolved fluorescence spectra obtained will be the subject of a future report. The

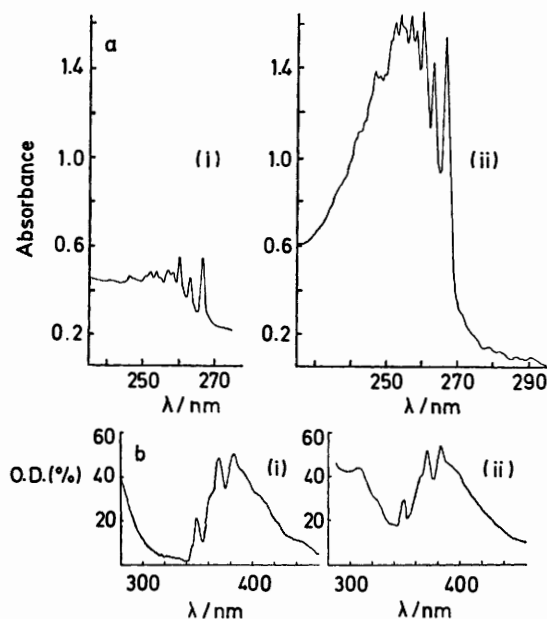
TABLE 1

S_0-S_n Absorption spectra for styrenes in perfluoromethylcyclohexane

	$\lambda_{\max.}(S_0-S_2)/$ nm	0-0 Band for S_0-S_1 transition (nm)
Styrene (1)	240.0	288.0
<i>trans</i> -1-Phenylpropene (2)	245.0	290.0
<i>cis</i> -1-Phenylpropene (3)	238.5	288.0
<i>trans</i> -1-Phenyl-3,3-dimethylbut-1-ene (4)	245.0	290.0
<i>cis</i> -1-Phenyl-3,3-dimethylbut-1-ene (5)	230.0	
2-Phenylpropene (6)	237.0	287.0
1-Phenylcyclopentene (7)	250.0	290.0
3-Phenylpropene (8)		267.0]

important point as far as this report is concerned, is that no phosphorescence was observed on direct excitation.

Triplet Sensitization Studies.—We devised a series of experiments in argon at 10 K using a range of ratios of toluene to phenylcyclobutene (PCB) (chosen because the rigid nature of this styrene derivative was expected to



a, (i) The absorption spectrum of toluene-argon (1 : 50) at 10 K (25 pulses); (ii) the absorption spectrum of toluene-PCB-argon (40 : 1 : 2000) at 10 K (60 pulses). b, (i) The phosphorescence spectrum produced by exciting mixture a(i) at 265 nm; (ii) the total emission spectrum produced by exciting mixture a(ii) at 265 nm

inhibit an important non-radiative relaxation route *i.e.* rotation about the essential double bond). The optically transparent matrices were deposited by the pulsed matrix isolation technique (p.m.i.)⁷ and monitored by u.v. spectroscopy (Figure a). The effect of phenylcyclobutene on the

⁷ M. M. Rochkind, *Science*, 1968, **160**, 196; see also R. N. Perutz and J. J. Turner, *J.C.S. Faraday II*, 1973, 452.

toluene triplet state was observed by measuring (a) the total emission spectra and (b) the toluene phosphorescence lifetimes (τ_p).

(i) *Toluene-Argon* [Matrix Ratio (M.R.) 1 : 50].—At this ratio little self quenching takes place since the observed τ_p was 12.8 ± 0.2 s, close to that observed by Johnson and Studer (12.6 ± 0.1 s) at M.R. 1 : 500.⁸

(ii) *Toluene-PCB-Argon* (40 : 1 : 2 000).—More than twice as many pulses of mixture were deposited in this experiment in comparison with (i) (see Figure a). However, a very similar intensity of toluene phosphorescence was observed (Figure b). Since it is experimentally very difficult to measure even relative emission quantum yields under these conditions, it would be dangerous to draw any conclusions from those differences in optical densities necessary to produce the same phosphorescence intensity. The two important points to note are that (a) apart from the contribution made by PCB fluorescence [probably due to direct absorption by PCB with perhaps some contributions from $^1(\text{Toluene})_1$ to $^1(\text{PCB})_0$ singlet energy transfer] the total luminescence is the result of toluene phosphorescence only, *i.e.* no new emissions; (b) the τ_p is reduced to 11.3 ± 0.3 s.

(iii) *Toluene-PCB-Argon* (20 : 1 : 1 000).—Under these

TABLE 2

S_0-T_1 Oxygen enhanced absorption spectra of some styrenes and 3-phenylpropene *

Compound	$\lambda_{\text{onset}}/\text{nm}$	S_0-T_1 $\lambda_{\max.}/\text{nm}$	$(S_2-T_1)_A$ $\Delta E/kJ$	$(S_2-T_1)_B$ mol^{-1}
(1)	463.0 (463.0) ^a	390.0	240	191
(2)	480.0 (478.0) ^b	400.0	239	189
(3)	435.0	385.0	234	191.5
(4)	460.0	395.0	228	186
(5)	435.0	390.0	243	213.5
(6)	460.0	385.0	243	193.5
(7)	480.0	410.0	229	187
(8)	355.0 ^c	326.0		

* Measured in perfluoromethylcyclohexane.

^a Data from ref. 13. ^b Data from ref. 14. ^c Data from ref. 10.

conditions τ_p was reduced further to 9.3 ± 0.3 s and the toluene phosphorescence spectrum was too weak to measure with our spectrofluorimeter.

Table 2 shows the data obtained from the oxygen enhanced S_0-T_1 absorption spectra of a series of styrenes and 3-phenylpropene in perfluoromethylcyclohexane. Also shown are the energy differences between the $\lambda_{\max.}$ of the S_0-S_2 band and the onset (taken as λ at 20% of $\lambda_{\max.}$) of the S_0-T_1 band $(S_2-T_1)_A$ and the differences between the $\lambda_{\max.}$ for the S_0-T_1 band and the $\lambda_{\max.}$ for the S_0-S_2 band $(S_2-T_1)_B$.

DISCUSSION

A straightforward approach to improving the resolution of the absorption spectra of solutions is to employ an inert solvent of low dielectric constant. This reduces solvent solute interactions and thus improves vibrational structure compared to a hydrocarbon solution. A further effect in going from a hydrocarbon to a fluorocarbon solvent is the differential solvent shifts of different electronic absorption bands and these shifts

⁸ P. M. Johnson and M. C. Studer, *Chem. Phys. Letters*, 1973, **18**, 341.

have been semi-quantitatively related to the oscillator strengths of the different transitions.^{8,9} This effect is observed in the styrenes studied in that a blue shift of 3–4 and 1–2 nm in going from cyclohexane to perfluoromethylcyclohexane solution is seen for the 1A_1 – 1A_1 and 1A_1 – 1B_2 bands respectively (in those cases where the 1A_1 – 1B_2 transition was resolved in cyclohexane) and leads to an increased separation of the two bands.

Although we knew of no reports of the observation of phosphorescence from a styrene and had attempted, in vain, to detect phosphorescence from acyclic styrenes in glasses at 77 K, we decided to look for phosphorescence under extreme conditions. Using very carefully purified styrenes in pure nitrogen matrices at 10 K and irradiating over a range of wavelengths from 250 nm to the long wavelength limits of absorption, fluorescence but no phosphorescence was observed for the five styrenes studied (see Experimental section). If we make the assumption that the quantum yield of fluorescence is at least 0.6 for phenylcyclobutene under these conditions (Zimmerman and his co-workers have obtained a value of ϕ_F of 0.6 at 77 K in a glass⁴), then under the conditions of our experiment, we could have detected phosphorescence with a quantum yield of $\phi_F \times 5 \times 10^{-3}$, *i.e.* 3×10^{-3} .

Clearly, the lack of phosphorescence on direct irradiation may be the result of an inefficient intersystem crossing or a T_1 – S_0 radiative rate constant small in comparison with the sum of the T_1 – S_0 non-radiative rate constants (*i.e.* a low phosphorescence efficiency). The toluene sensitization experiments provide some important evidence on this point. Toluene has a high intersystem crossing efficiency [ϕ_p (argon crystals at 20 K) 0.47]⁸ and a lowest triplet state higher in energy (344.5 kJ mol⁻¹) than that of any simple styrene derivative (see later). Thus, although there is extensive overlap in the S_0 – S_n absorption spectra of toluene and phenylcyclobutene it was decided to use this pair for a triplet sensitization experiment. The concentrations were chosen such that the toluene absorbed as much light as possible but that the concentration of the phenylcyclobutene was high enough to allow efficient energy transfer from the T_1 state of toluene to the triplet state(s) of phenylcyclobutene. Under these conditions, fluorescence from the phenylcyclobutene was observed and toluene phosphorescence was quenched but no new long wavelength emission was observed (Figure b).

The quenching of toluene phosphorescence is probably the result of both singlet and triplet energy transfer from toluene to PCB. This is evidenced by the very rapid fall off in toluene phosphorescence intensity while the toluene triplet lifetime decreases much more slowly with added PCB. However the decrease in τ_p provides unambiguous evidence of triplet quenching, and the

⁸ N. S. Bayliss, *J. Chem. Phys.*, 1950, **18**, 292.

¹⁰ J. Metcalfe, M. G. Rockley, and D. Phillips, *J.C.S. Faraday II*, 1974, 1660.

¹¹ D. F. Evans, *Nature*, 1956, **187**, 534; D. F. Evans, *J. Chem. Soc.*, 1959, 2753.

lack of any new emission bands clearly indicates that within the sensitivity limits of experiments PCB triplets do not emit. We thus conclude that the lack of phosphorescence from styrenes on direct irradiation may be the result of both inefficient intersystem-crossing and the presence of an efficient non-radiative relaxation from T_1 . It is interesting to speculate on this non-radiative relaxation process. Clearly for cyclic styrene derivatives in glasses or matrices at low temperatures, the most obvious non-radiative process, rotation about the olefinic double bond, must be very inefficient. Thus other non-radiative process(es) may be important. However, in the absence of any unambiguous evidence, discussion of the nature of these processes must be deferred.

The technique of oxygen enhanced S_0 – T_n absorption is perhaps the most convenient method of determining the triplet state energy levels of non-phosphorescent molecules.^{10,11} In the case of molecules studied here, the gas-phase technique could not be used because of the low vapour pressures of some styrenes. Thus the solution-phase spectra were studied and perfluoromethylcyclohexane was chosen as the solvent for the following reasons: (i) to minimise the possibility of explosions; (ii) to obtain the best resolution of the S_0 – T_n spectra; and (iii) oxygen is more soluble in low molecular weight fluorocarbons than in chloroform or carbon tetrachloride, other solvents which have been used in this type of experiment.¹²

We were able to reproduce the S_0 – T_1 absorption spectra of styrene reported by Evans¹³ and our value for the onset of absorption for *trans*-1-phenylpropene is very close to the value reported by Lamola and Hammond (250.0 kJ mol⁻¹).¹⁴ However, the estimate of 275.0 kJ mol⁻¹ made for the planar triplet of *cis*-1-phenylpropene is too high.¹⁵

It can be seen that while there is no simple correlation in the S_0 – T_1 splitting for the series, the $(S_2$ – $T_1)_A$ splitting for the *trans*-isomers (2) and (4) and the cyclic derivative (7) is the same to within experimental error (187.5 ± 1.5 kJ mol⁻¹). Also for all styrenes studied, with the exception of the very sterically hindered compound (5), the $(S_2$ – $T_1)_B$ splitting is approximately constant at 189.5 ± 4 kJ mol⁻¹. This strongly suggests a correlation in electronic configuration between the S_2 and T_1 , a exception of the very sterically hindered species (5), the $(S_2$ – $T_1)_A$ splitting is approximately constant at 189.5 ± 4 kJ mol⁻¹. This strongly suggests a correlation in electronic configuration between the S_2 and T_1 , a feature of the styrenes already suggested by us. Furthermore, we feel confident that the maximum for the S_0 – T_1 absorption spectrum can be predicted accurately for most simple styrene derivatives from a

¹² J. E. Jolley and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1958, **80**, 1050.

¹³ D. F. Evans, *J. Chem. Soc.*, 1957, 1351.

¹⁴ A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 1965, **43**, 2129.

¹⁵ R. A. Caldwell, G. W. Sovocool, and R. J. Peresie, *J. Amer. Chem. Soc.*, 1973, **95**, 1496.

measurement of the S_0 - S_2 maximum and that the 'lowest' vibrational level of the T_1 state can also be obtained [since $(S_2-T_1)_A = 235.5 \pm 7.5$ kJ mol⁻¹]. The approximate nature of the latter relationship almost certainly reflects the difficulties of determining $\lambda_{(\text{onset})}$ in the S_0 - T_1 absorption spectrum rather than any real variation in energies of the vibrationless triplet states.

For reasons of comparison and because of our interest in the di- π -methane rearrangement¹⁶ of 3-arylpropene derivatives, we also determined the S_0 - T_1 absorption spectrum of 3-phenylpropene (8). The important conclusion that can be reached from our results is that the energy of the lowest vibrational level of T_1 in (8) (344.5 kJ mol⁻¹) is identical with the T_1 energy of toluene (344.5 kJ mol⁻¹)¹⁰ and, within experimental error, the T_1 level of ethylene (343.5 kJ mol⁻¹).¹⁷ Here it is assumed that even if the 0-0 band is not observable in ethylene because of the effects of the considerably different C=C bond lengths in the ground state and T_1 state, then it may be assumed that approximately the same Franck-Condon factors would apply to the transition in (8), involving the production of an excited triplet state with energy localisation on the olefinic system. Thus, any interaction between the two π systems in (8) is not reflected in the S_0 - S_1 or the S_0 - T_1 energy gaps. However, there certainly is coupling between the two nearly isoenergetic triplets. This is demonstrated by the observation of efficient geometric isomerization about the double bond on excitation at the 0-0 band of the 1A_1 - 1B_2 transition in 1-phenylbut-2-ene.

EXPERIMENTAL

Materials.—Toluene, styrene, *trans*-1-phenylpropene, and 2-phenylpropene were purchased. 1-Phenylcyclobutene, 1-phenylcyclopentene, and *trans*-3,3-dimethyl-1-phenylbut-1-ene were synthesised by standard methods. *cis*-1-Phenylpropene and *cis*-3,3-dimethyl-1-phenylbut-1-ene were obtained from the *trans*-isomers by photosensitization using fluorenone (p.s.s. ca. 85% *cis*-isomer) in cyclohexane.¹⁵

In every case, purification was carried out using high vacuum bulb-to-bulb distillation followed by preparative g.l.c. on a 15 ft 15% QFI column (support Chromosorb G AW, DMCS treated). In this way, impurity levels were always kept below 0.2%.

Perfluoromethylcyclohexane was Flutec grade PP2. It showed no evidence of hydrogen containing material above a level of 0.2% (detection limit by our n.m.r. analysis). It was passed through an alumina column before use and after this treatment showed no absorption in the region of interest, *i.e.* above 230 nm. B.O.C. Grade X nitrogen and argon were used in the matrix luminescence studies.

Equipment and Techniques.—The cell used for obtaining the S_0 - T_1 absorption spectra have been described previously.¹⁰ A solution (ca. 10 cm³, ca. 10⁻²M) of the styrene in perfluoromethylcyclohexane was placed in the high pressure cell and the cell attached to the high pressure system. A spectrum of the solution subjected to one atmosphere of oxygen was obtained to provide a reference. The system was then pressurised to 180 atm. of oxygen, left for 30 min to equilibrate, and then three spectra obtained. S_0 - T_1 Absorption spectra were obtained by averaging and subtracting the reference. Data points were taken every 5 nm except near the maxima and the onsets where points every 2 nm were taken. To avoid a build-up of background absorption due to polymeric material, the cell was thoroughly washed between spectra and after every five fillings was completely dismantled and cleaned. The spectrometer used for obtaining the S_0 - T_1 and most of the S_0 - S_n absorption spectra was a Pye-Unicam SP 1800B.

A more complete description of the matrix technique will be given in a future publication and so only a brief outline will be given here. All experiments were performed at 10 K using an Air Products Displex CSA-202 closed cycle helium refrigeration system. All matrices were deposited by the pulsed method of Rochkind,⁷ using LiF central windows. Two LiF outer windows were used to measure the u.v. absorption and one LiF and one Spectrosil outer window used in the luminescence studies. The gaseous mixtures of toluene-argon (1 : 50) and toluene-PCB-argon (40 : 1 : 2 000 and 20 : 1 : 1 000) were made up by standard manometric technique and stored in a blackened bulb. A Farrand Mark I spectrofluorometer was used for the matrix luminescence studies.

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¹⁶ R. C. Cookson, A. B. B. Ferreira, and K. Salisbury, *J.C.S. Chem. Comm.*, 1974, 665.

¹⁷ D. F. Evans, *J. Chem. Soc.*, 1960, 1753.