The Photochemistry of 1-Phenylpropenes

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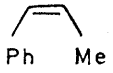
An examination of the photochemical and photophysical processes resulting from excitation in the α and A bands of *cis*- and *trans*-1-phenylpropene in the gas phase has been carried out. Measurement of quantum yields of fluorescence, fluorescence lifetimes, and quantum yields of isomerization on excitation in the α bands has revealed that the value for the sum of the non-radiative processes in this first excited singlet state (Σk_{NR}) is the same for both isomers. A consideration of the potential energy diagrams for the ground state and first two excited singlet and triplet states strongly suggests that geometric isomerization is solely a triplet process for excitation in the α bands. This in turn implies that the major contribution to Σk_{NR} for each isomer is the intersystem crossing rate constant. In contrast to observations made on solutions of monophenylalkenes, excitation in the A bands of the phenylpropenes does not lead to efficient geometric isomerization. Polymerization is the major detectable process.

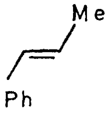
THE photochemistry of stilbene and its derivatives has been a centre of interest for decades and many aspects of their photochemistry are now understood.[1-3] In contrast the photochemistry of the structurally and spectroscopically simpler conjugated monophenylalkenes have been studied to a limited extent and then only qualitatively.[4] The need for an understanding of the simple processes of geometric isomerisation and fluorescence becomes obvious when it is realised that the styryl chromophore is present almost as frequently as the ubiquitous carbonyl group as the light-absorbing chromophore of complex molecules whose photochemistry is at present under scrutiny.

At the outset there seemed to be two important questions. What are the important primary photochemical processes resulting from excitation in the long wavelength band (α band)[5] and are these the same processes that are important on excitation in the intense second band (A band)?[5]

The 1-phenylpropenes (1) and (2), as the simplest phenylalkenes capable of undergoing easily detectable geometric isomerisation and because of their volatility, were chosen for this study and the investigation was carried out on the vapours of (1) and (2). Thus in the first instance solvent effects were avoided.



(1)



(2)

RESULTS

The absorption spectra of *cis*- and *trans*-1-phenylpropene (1) and (2) exhibit two bands above 220 nm. The long wavelength bands referred to as the α, ^1L_b, or B band, showing well defined vibrational structure, have been attributed to a transition to an unoccupied MO localised on the aromatic ring and only slightly perturbed by the adjacent olefinic group. However there certainly is some perturbation as is seen from the difference in the extinction coefficients for the two isomers (Table 1).

The second band described as the A, ^1L_a, or K band corresponds to the one electron transition, $\psi + 1$ to $\psi - 1$, in the LCAO–MO[5] method and is predicted to be very dependent (in wavelength and intensity) upon the interaction of the aromatic and olefinic groups. This is shown in the sensitivity of this band to the angle of twist β[5,6] about the C–C bond between the planes of the *p* orbitals of the two groups. The differences in the A band of the two isomers (1) and (2) give a qualitative indication of this effect.

TABLE 1

Electronic absorption spectra of (1) and (2)[a]

	α Band (λ/nm)	A Band (λ/nm)
(1)	289·0 (ε 218)	238·0 (ε 12,714
	278·0 (ε 387)	
	290·0 (ε 727)	
(2)	282·0 (ε 1020)	248·0 (ε 18,300)
	273·0 (ε 1202)	

[a] Measured in cyclohexane.

Table 2 shows the fluorescence quantum yields of (1) and (2) as functions of wavelength.

TABLE 2

Fluorescence quantum yields of (1) and (2)[a]

λ/nm[b]	(1)[c]	(2)[c]
290		0·22 ± 0·02
285	0·060 ± 0·010	0·21 ± 0·02
280	0·070 ± 0·010	0·21 ± 0·02
275	0·050 ± 0·005	0·21 ± 0·02
265	0·005 ± 0·004	0·065 ± 0·010
255	<0·002	0·010 ± 0·005
250	<0·002	<0·002

[a] All measurements were made on 0·1—0·5 mmHg of the phenylpropenes. 5 mmHg of n-butane added to (1) and (2) at each wavelength produced no measureable effect. [b] Bandwidth 1·2 nm. [c] Quantum yields were measured relative to that of benzene (1 mmHg) irradiated at 254 nm (ϕ_f 0·18) (W. A. Noyes, jun., W. A. Mulac, and D. A. Harter, *J. Chem. Phys.*, 1966, **44**, 2100) and after due consideration it was found that corrections for the differences in the sensitivity of the photodetectors at the wavelengths of excitation and emission were not necessary.

The two points to be noted from these fluorescence quantum yield measurements are: 1, the quantum yields

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[3] J. Saltiel, *J. Amer. Chem. Soc.*, 1968, **90**, 6394.

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on excitation in the α bands of both isomers remain approximately constant throughout the α bands but fall to zero on excitation in the A bands, and 2, the fluorescence quantum yield of the *trans*-isomer (2) is approximately three times that of the *cis*-isomer (1) on excitation in the α bands.

The difference in the values of $\phi_{f(1)}$ and $\phi_{f(2)}$ *a priori* can be explained by differences in the radiative rate constants ($k_{R(1)}$ and $k_{R(2)}$), by differences in the non-radiative rate constants ($\Sigma k_{NR(1)}$ and $\Sigma k_{NR(2)}$), or by differences in both rate constants. The radiative rate constants for fluorescence from the first excited singlet states of benzene derivatives can be calculated from the integrated absorption bands by one of several methods available.[7] However, in this case, because of the extensive overlap with the A bands integration is not possible. Comparison of the peak heights of the two longest wavelength bands within the α band envelopes of the two isomers is likely to give approximate relative radiative lifetimes. Taking the mean of these ratios we can estimate that $k_{R(2)}/k_{R(1)} = 3{\cdot}0$. This would certainly suggest that the difference between the fluorescence quantum yields of (1) and (2) is due only to a difference in the k_R values.

TABLE 3

Fluorescence lifetimes and radiative and non-radiative rate constants for (1) and (2) [a]

	(1)				(2)		
λ/nm [b]	τ/ns [c]	$10^{-6}k_R/s^{-1}$	$10^{-7}\Sigma k_{NR}/s^{-1}$	$\frac{k_R\ (2)}{k_R\ (1)}$	τ/ns	$10^{-7}k_R/s^{-1}$	$10^{-7}\Sigma k_{NR}/s^{-1}$
292					16·4	1·31	4·78
285	17·0	3·8	5·5	4·0	13·8	1·52	5·78
280	16·0	4·4	5·8	3·7	13·0	1·62	6·07
275	13·7	3·7	6·9	4·5	12·5	1·68	6·32
265	9·6	2·0	10·2		6·8	0·99	13·7
255					1·0	1·38	124·1

[a] 0·5 mmHg of (1) and 1·0 mmHg of (2) were used in the lifetime measurements. [b] An excitation bandwidth of 1 nm was used. [c] The mean deviation for lifetimes of 10 ns or more is 2—5% while for lifetimes below 10 ns the error rapidly increases.

In order to obtain much more precise information about the processes emanating from the first excited singlet states of these two isomers, the low pressure fluorescence lifetimes were measured using a single photon counting technique.[8] Table 3 gives the values for the fluorescence lifetimes which have been used together with the quantum yields of fluorescence of Table 2 to calculate values of k_R and Σk_{NR} in each case.

From Table 3 it is quite clear that our conclusions concerning the constancy of the sum of the non-radiative rate constants from the first excited singlet states of the two isomers are quantitatively confirmed. Furthermore it can be seen that a rapid increase in the rate constants for some non-radiative process(es) is the reason for the rapid fall in fluorescence quantum yields as the excitation wavelength moves from the α band into the A band.

The fluorescence quenching of (1) and (2) by n-butane and by buta-1,3-diene was semi-quantitatively investigated. For n-butane addition to the *trans*-isomer (2) irradiating at 290·0 nm no effect was seen up to 300 mmHg of added gas. fluorescence quenching of (2) by the diene was seen and the half-quenching pressure ($\phi_{f_0}/\phi_f = 2$) of 360 mmHg was obtained. While the Stern–Volmer plots for (2) were reproducible, this was not the case with the *cis*-isomer. On addition of the n-butane or the diene to (1) the fluorescence measurements were very scattered and no satisfactory result could be obtained. The propensity of the *cis*-isomer to polymerise was noted to be considerably greater than the *trans*-isomer in all the experiments carried out. This observation has some analogies in the photochemistry of more complex aryl olefins.

Geometric Isomerisation.—The results of an investigation of the geometric isomerisation of (1) and (2) on direct irradiation are interesting and are shown in Table 4.

The considerable errors in these quantum yields must be attributed partly to the problems of measuring the light absorbed by the vapours in a cell which becomes coated with polymer (see Experimental section) and partly to the g.l.c. analysis.

TABLE 4

Quantum yields of geometric isomerisation of (1) and (2) [a]

	(1)	(2)
ϕ (285 nm) [b]	$0{\cdot}33 \mp 0{\cdot}06$	$0{\cdot}22 \mp 0{\cdot}06$
ϕ (250 nm)	$\leqslant 0{\cdot}05$	$\leqslant 0{\cdot}05$

[a] Pressures used for photolysis were 1·0—2·0 mmHg. [b] A bandwidth of 2·0 nm was used at both wavelengths.

DISCUSSION

For the purposes of the discussion it will be useful to construct a potential energy diagram for the first two electronically excited singlet and triplet states of the phenylpropenes (Figure) as a function of the angle of twist (θ) about the olefinic double bond.

The first excited singlet state may be considered to involve excitation (π–π^*) localised on the aromatic ring. Now Lombardi and Parker,[10] utilising the Stark effect, have shown that there is little if any increased interaction between the double bond and the benzene ring on excitation in the α band of styrene. Therefore, in an approximate analysis, we can treat the change in energy of the first excited singlet state on rotation about the double bond as the sum of the change in energies of the π–π^* transition on the aromatic ring and the change in energy of what may be considered a ground state double bond. Since the origin of absorptions of (1) and (2) is very close to that of benzene (260·0 nm) [11] we expect only a small increase in energy as $\theta \longrightarrow \pi/2$ for

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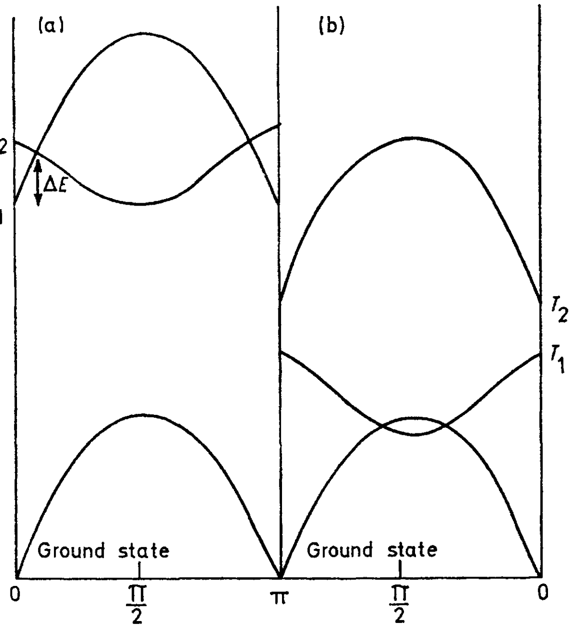
[10] H. Parker and J. R. Lombardi, *J. Chem. Phys.*, 1971, **54**, 5095.

[11] W. W. Robertson, J. F. Music, and F. A. Matsen, *J. Amer. Chem. Soc.*, 1950, **72**, 5260.

this transition. However, rotation about the double bond may be considered to require the same activation energy (160—190 kJ mol^{-1})[12] as is necessary for thermal isomerisation. Setting the 0–0 level for this first excited singlet state at *ca.* 410 kJ mol^{-1} for both (1) and (2) an approximate potential energy curve can be constructed as is shown in the Figure. The dependence of the energy of the second excited singlet state upon θ is likely to be of a very different form. Thus, due to electron–electron interaction in this state it can be predicted that there will be a decrease in energy just as was calculated for ethylene[13] and stilbene.[2] Until we carry out a complete calculation we can only estimate the potential energy minimum as 50—100 kJ mol^{-1}. Setting the 0–0 level for the A band at *ca.* 485 kJ mol^{-1} an approximate potential energy curve may be constructed.



Potential energy diagram for 1-phenylpropene as a function of θ: (a) ground state and excited singlet manifold; (b) ground state and triplet manifold

Turning to the triplet manifold, it can be seen immediately that the energy levels (for the planar molecule) will be reversed. Thus the localised aromatic triplet may be expected to lie at 290—330 kJ mol^{-1}, certainly higher in energy than the 'conjugated' triplet. The latter excited state has been shown to have a vertical excitation energy of 250 kJ mol^{-1} [14] with a twisted state at least 30 kJ mol^{-1} lower in energy.[4b] To confirm the general features of these potential curves we are carrying out SCF–MO calculations of the type already shown to be reasonably successful in this area.[2]

Excitation in the α Band.—Excitation in this band results in fluorescence and in geometric isomerisation. The question then arises: is isomerisation the result of intersystem crossing to the triplet manifold and subsequent relaxation to the twisted triplet state or does isomerisation occur by relaxation of a twisted singlet state to the ground state?

Singlet Mechanism.—For the singlet mechanism to be in operation, a crossing from the 'aromatic' singlet state energy surface to the 'conjugated' singlet state must occur. However, an inspection of the potential energy curve for the first excited singlet state of the olefins clearly indicates the presence of a potential energy barrier to rotation. The size of the barrier can be better assessed when we know the position of the crossing point of the two excited singlet states but it is probably less than the difference between the 0–0 bands of the first two excited singlet states (*ca.* 75 kJ mol^{-1}). The difference between the 0–0 level of the α band and the onset of the A band in the absorption spectra may be taken to give a good indication of this activation energy (ΔE) for crossing to the second excited singlet state. From the gas phase spectra this is found to be 40 and 50 kJ mol^{-1} for the *cis*- and *trans*-isomers respectively. Thus it seems very unlikely that isomerisation occurs to any great extent within the singlet manifold, on excitation to low vibrational levels of the first excited singlet state.

Triplet Mechanism.—If the triplet mechanism obtains then we may conclude that k_{isc} (the intersystem crossing rate constant) is the major or perhaps the only contributer to Σk_{NR} for both isomers.

That $\Sigma k_{NR(1)} = \Sigma k_{NR(2)}$ lends further support for the triplet mechanism since as already stated, the characteristics of the α band suggest that the 'aromatic' singlet state is only slightly perturbed by the neighbouring double bond.

Much remains to be learned about the effects of the structure of benzene derivatives on the rates of intersystem crossing from the $^1B_{2u}$ type singlet. However, the value of 6×10^7 s^{-1} for the intersystem crossing rate constant is within an order of magnitude of the value for some monosubstituted benzene derivatives k_{isc}(toluene)[15] $= 2 \times 10^7$ s^{-1} but k_{isc}(phenylcyclopropane)[16] $< 8 \times 10^6$ s^{-1}.

Geometric isomerisation *can* occur from the triplet manifold as is indicated by Figure (b) and is supported by triplet sensitisation experiments carried out in solution.

If a branching ratio [k(twisted triplet) $\longrightarrow$ *cis*/k(twisted triplet) $\longrightarrow$ *trans*] of 1 is assumed then it can be seen that there is a quantum deficiency of *ca.* 0·25 in the case of (1) and 0·35 for (2). This can only be attributed to radiationless processes, the most important of which is probably polymerisation, although other processes cannot be ruled out.[17] The short lifetime of the first excited singlet state and the low pressures used

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[12] R. B. Cundall, *Progr. Reaction Kinetics*, 1964, **2**, 165.

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in the experiments taken together indicate that polymerisation must occur only after intersystem crossing to the triplet manifold.

Excitation in the A *Band*.—Excitation in this band resulted in some geometric isomerisation, much polymerisation, and no detectable emission. Small amounts of unidentified products were detected at large conversions of the isomers. It can only be assumed that under the low pressure conditions the unimolecular decomposition to radicals competes efficiently both with inter- and intra-molecular relaxation to the twisted state and with internal conversion to the first excited singlet state.

Comparison with Solution Studies.—In a recent study of the photochemical geometric isomerisation of the isomeric 1,5-diphenylpenta-1,4-dienes Block and Orf suggest that geometric isomerisation on excitation in the A bands, which is observed to be efficient, is a singlet process,[9] while excitation in the α band leads to polymerisation as a result of intersystem crossing and the reaction of long lived triplets (biradicals).

At first sight these results may seem incompatible with our own. However, a consideration of the very different conditions of the photolyses gives a viable rational. On excitation in the A band in solution, unlike the situation in the gas phase at low pressure, rapid collisional relaxation is possible and so the twisted 'conjugated' singlet state may be populated. On the other hand on excitation in the α band, intersystem crossing may be efficient, but, unlike the gas phase photolysis the triplets formed may collide with other molecules and thus initiate polymerisation.

EXPERIMENTAL

Materials.—*trans*-1-*Phenylpropene* (2) was obtained from several different sources but samples supplied by Aldrich proved satisfactory. The *trans*-isomer was photoisomerised to the *cis*-isomer using acetonaphthone in hexane. Both isomers were purified by preparative g.l.c. using a 5 ft × 0·125 in 10% OV 1 on silanised Chromosorb G (60—80 mesh) or a 15 ft × 0·25 in 20% FFAP on Chromosorb P (45—60 mesh). No sample of (1) or (2) was used unless the impurity level was $<0{\cdot}2\%$.

Benzene, n-butane, and buta-1,3-diene were Phillips research grade and were used without further purification.

Absorption and Emission Spectroscopy.—Solution and gas phase absorption spectra were measured using a Unicam SP 700 instrument. Emission spectra were measured with a Farrand spectrofluorimeter mark I. The experimental arrangement for measuring the quantum yields of fluorescence has been described.[18] Calculations of the correction factors for these quantum yields based on the differences in the wavelengths of absorption and emission of the benzene standard and the phenylpropenes showed that the correction was $<3\%$ and since this is little more than the uncertainty in the calculation no correction was applied.

The single photon counting technique used for measuring the fluorescence lifetimes has been described.[8]

Photolysis.—The quantum yields of photolysis were obtained essentially as described earlier.[18] Actinometry was carried out using the potassium ferrioxalate method,[19] making corrections for the optics of the systems used.[20] In addition it was necessary to make corrections for light absorbed by a small amount of polymer built up during a photolysis. This polymer formation was minimised by working to low conversions, *i.e.* $\leqslant 1\%$, and since the vapours of (1) and (2) absorbed $>70\%$ of the incident light it was assumed that all the polymer was formed on the front face of the cell. Therefore the build up of polymer was treated as if it were a decrease in light intensity incident on the cell.

Analysis of the products was carried out using g.l.c. Either a 50 ft × 0·02 in 1,3-bis-(*m*-phenoxyphenoxy)-benzene on Apiezon L Golay or a 20 ft × 0·125 in 10% OV 1 on Chromosorb G column (D.M.C.S. treated) was used. An internal standard of t-butylbenzene was used. Corrections were made for the presence of very small amounts of the geometric isomer in the starting materials.

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