

## Short Communication

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### Quenching of the fluorescence of styrenes by ground state oxygen

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The primary photochemical and photophysical processes of styrenes continue to be a centre of interest<sup>1,2</sup>, as do their secondary processes and with the photopolymerization of styrenes and related molecules now under investigation<sup>3,4</sup> it is imperative that the simple primary unimolecular and bimolecular processes of electronically excited styrenes be understood.

The interaction of the ubiquitous ground state oxygen with electronically excited styrenes was studied to make comparisons with alkylbenzenes and to obtain detailed information about the possible effects of oxygen in the photopolymerization of styrenes.

*Cis*- and *trans*-1-phenylprop-1-ene (1 and 2) have two absorption bands above 230 nm, a long wavelength structured band ( $\alpha$  band)<sup>5</sup> resulting from excitation localized on the aromatic ring and a shorter wavelength intense band (A band)<sup>5</sup> associated with excitation delocalized over the styryl moiety. Excitation in the  $\alpha$  band at low pressures in the gas phase results in efficient fluorescence (excitation at 285 nm,  $\Phi_F(1) = 0.06$ ;  $\Phi_F(2) = 0.21$ )<sup>2</sup> while excitation in the A band does not lead to fluorescence<sup>2</sup>.

In the present study 1 and 2 were excited at  $285 \pm 2$  nm, near the O-O vibrational bands of the  $\alpha$  band<sup>1</sup>, and the fluorescence efficiency monitored as a function of added oxygen. A 5 cm path-length quartz cell was employed and was attached to a conventional high vacuum system. Polymer which was built up on the optical flats during the experiment was burnt off in a stream of air. The use of acids to clean the cell was avoided since in an acid washed cell the polymerization was accelerated. Details of the optical set up have been given elsewhere<sup>6</sup>. Figure 1 shows the Stern-Volmer plots for fluorescence quenching by oxygen. From these plots the quenching rate constants can be determined.

$$\Phi_F/\Phi_{Fq} = 1 + k_q \tau_0 [O_2]$$

where  $\Phi_F$  = quantum yield of fluorescence in the absence of oxygen,  $\Phi_{Fq}$  = quantum yield of fluorescence in the presence of oxygen,  $[O_2]$  = oxygen concentra-

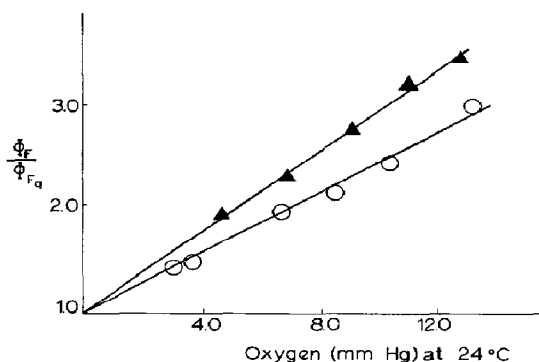


Fig. 1. The quenching of the fluorescence of 1(O) and 2( $\blacktriangle$ ) by oxygen.

tion,  $\tau_0$  = lifetime of the first excited singlet states of the phenylpropenes in the absence of oxygen,  $\tau_0(1) = 1.7 \times 10^{-8}$  s (ref. 2),  $\tau_0(2) = 1.4 \times 10^{-8}$  s (ref. 2). From the Stern-Volmer plots and converting pressures into concentrations of molecule  $\text{cm}^{-3}$ :

$$k_q(1) = 2.7 \times 10^{-10} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_q(2) = 4.24 \times 10^{-10} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$$

These values may be compared with  $k_q = 4.2 \times 10^{-10} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$  for t-butylbenzene and  $k_q = 3.7 \times 10^{-10} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$  for ethyl benzene<sup>7</sup>.

Evidence has been presented to indicate a weak charge transfer complex between first excited singlet states of aromatics and ground state oxygen<sup>8</sup>. Brewer obtained a good correlation between  $\log k_q$  versus the first ionization potentials for a series of alkyl- and fluoro-benzenes excited to their first excited singlet states and it was therefore of interest to determine whether the phenylpropenes would fall on the same straight line. The first ionization potentials of 1 and 2 were therefore determined using a Perkin-Elmer PS 16 Photoelectron Spectrometer and found to be 8.45 eV and 8.32 eV respectively. From Fig. 2 it can be seen that 1 and 2 deviate considerably from the relationship found to hold for the molecules studied by Brewer.

The reason for this deviation and the difference between  $k_q$  for the *cis* and *trans* isomers is not immediately obvious but the following arguments are put forward. Calculations of the collisional frequency of  $^3\text{O}_2$  and the phenylpropenes (assuming  $\sigma(\text{O}_2) \simeq 3.5 \text{ \AA}^2$  and  $\sigma(1 \text{ and } 2) \simeq 7.5 \text{ \AA}^2 \therefore \sigma(\text{mean}) = 5.5 \text{ \AA}^2$ ) show that the value of  $k_q(2)$  is very close to the collisional rate, as is the case for t-butylbenzene. Thus, the value for  $k_q$  for a series of molecules may reach a limit controlled by the collisional frequency and the ionization potentials and lower ionization potentials may have no further effect. As for the relatively low value for  $k_q$  for the *cis*-phenylpropene, we can rule out steric effects as being important since  $k_q$  for t-butylbenzene is  $4.2 \times 10^{-10} \text{ molecule}^{-1} \text{ cm}^{-3} \text{ s}^{-1}$ . We are therefore forced to look for electronic factors and suggest that in the *cis* isomer, with its more

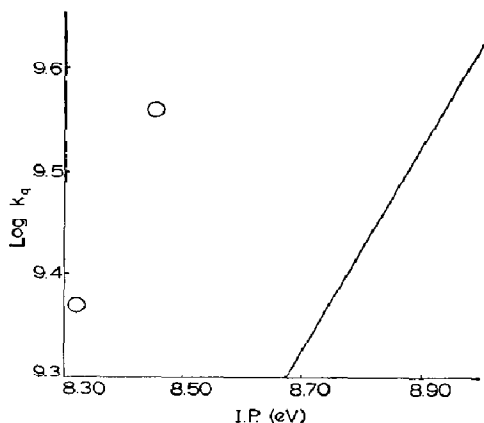


Fig. 2. The relationship between ionization potential and  $\log k_q$  for 1 and 2 (○) and some alky and halogeno benzenes.

twisted geometry some small charge transfer interaction takes place between the donor excited aromatic ring and the double bond acceptor. Thus the oxygen is competing with the double bond for electron donation from the aromatic ring. An examination of the Stark effect in styrene on excitation in the  $\alpha$  band indicates that there is little if any increased interaction between the aromatic ring and the double bond as compared to the ground state interaction<sup>10</sup>. However, in styrene, as in the *trans*-phenylpropene(2), the aromatic ring and the double bond are nearly coplanar. It is therefore of interest to look for Stark effects in twisted styrene derivatives and also to look for anomalous decreases in  $k_q$  for styrenes with electron deficient double bonds.

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