

Short Communication

Effect of azulene on the direct and benzil-sensitized photoisomerization of 2-styrylthiophene

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1. Introduction

In the course of our investigation to determine the influence of the groups bonded to ethylenic double bonds on the mechanism of photoisomerization, we studied the photoisomerization of 2-styrylthiophene ($C_6H_5-CH=CH-C_4H_3S$) (STP) [1] and of α -phenyl- β -(2-thienyl)-acrylonitrile (PTA) [2]. For PTA a singlet pathway of direct photoisomerization was proposed on the basis of the different effect of azulene on the direct and sensitized processes; for STP the results obtained in the sensitized and direct irradiation and in the quenching of the benzophenone phosphorescence and triphenylene fluorescence were consistent with a mechanism where a cross-over of the singlet and triplet pathways occurred, the direct photoisomerization occurring through a triplet twisted state.

In the present paper we aim to verify the mechanism proposed for STP by an investigation of the effect of azulene on the direct and benzil-sensitized photoisomerization of this compound.

2. Experimental details

Trans and *cis* STP were prepared as previously reported [1]. The experimental equipment for irradiation, for measuring the incident light and for obtaining the spectra was the same as that described previously [3].

In the direct photoisomerization experiments in the presence of azulene the conditions were as follows: [STP] = 1.7×10^{-3} M; [azulene] = $3 \times 10^{-3} - 10^{-2}$ M; λ_{exc} = 365 nm.

The quantum yields were calculated from the kinetics of the photoisomerization in both directions and from the composition of the photostationary state by applying Zimmerman's method [4]. The light was corrected for azulene absorption, whereas the absorption of the azulene emission by STP was negligible.

In the sensitized photoisomerization the conditions were as follows: [STP] = [azulene] = $(1 - 4) \times 10^{-3}$ M; [benzil] = 0.005 M; λ_{exc} = 405 nm. At these concentrations the quantum yields in the absence of quencher have

constant values very close to those of the limiting quantum yields ($\Phi_{t \rightarrow c} = 0.55$; $\Phi_{c \rightarrow t} = 0.44$). The quantum yields were calculated from the initial conversion (up to 10%). The composition of the mixture was determined spectrophotometrically at 365 nm ($\epsilon_t = 330$; $\epsilon_c = 140$; $\epsilon_{az} = 27$; $\epsilon_{benzil} = 70$). In the experiments considered the absence of decomposition products was controlled by high pressure liquid chromatography using a Varian model 5000 instrument.

In direct and in sensitized irradiation starting with the *trans* isomer the photostationary state was attained by extrapolation, since the decomposition reactions were recorded after prolonged *cis* isomer irradiation.

All experiments were carried out with benzene solutions carefully deaerated by a nitrogen stream.

3. Results and discussion

Under direct irradiation at 365 nm, the *trans* \rightarrow *cis* quantum yield $\varphi_{t \rightarrow c}^q$ of photoisomerization of STP, determined in the presence of azulene quencher Q, decreased as the quencher concentration increased. The *cis* \rightarrow *trans* quantum yield $\varphi_{c \rightarrow t}^q$ determined under the same conditions was constant, indicating that the excited states of the *cis* isomer do not interact with azulene. The ratio of the *cis*-to-*trans* isomer concentrations at the photostationary equilibrium was that expected on the basis of the quantum yield values and of the extinction coefficients, *i.e.* it shifted in favour of the *trans* isomer as the concentration of azulene increased (Fig. 1). The relative values of the extinction coefficients of STP and azulene do not allow us to increase the quencher concentrations further to establish whether there is a residual quantum yield. In fact, at higher quencher concentrations the light absorbed by the azulene would be considerable and the intensity of fluorescence not negligible; in consequence, the quantum yields could not be correctly evaluated.

It was found that the ratio between the quantum yield $\varphi_{t \rightarrow c}$ in the absence of quencher and $\varphi_{t \rightarrow c}^q$ can be considered as a linear function of the azulene concentration (Fig. 2). The linearity of this plot is in accordance with the relation

$$\frac{\varphi}{\varphi^q} = 1 + K[Q]$$

expected for a reaction mechanism involving one state which is quenchable by azulene and responsible for the isomerization [5, 6]. In the above relationship, $K = k_q \tau$, where k_q is the quenching constant and τ is the lifetime of the quenchable state. In Fig. 2, the intercept is equal to unity and the slope is 50; because the slope yields the value of K , the lifetime of the state quenched by azulene in the direct irradiation is approximately equal to 5×10^{-8} s, given that $k_q \approx 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

Under limiting quantum yield conditions, both quantum yields $\Phi_{t \rightarrow c}^q$ and $\Phi_{c \rightarrow t}^q$ of the benzil-sensitized photoisomerization decreased as the azulene concentration increased. The ratio $\Phi_{t \rightarrow c} / \Phi_{t \rightarrow c}^q$ was a linear function of the

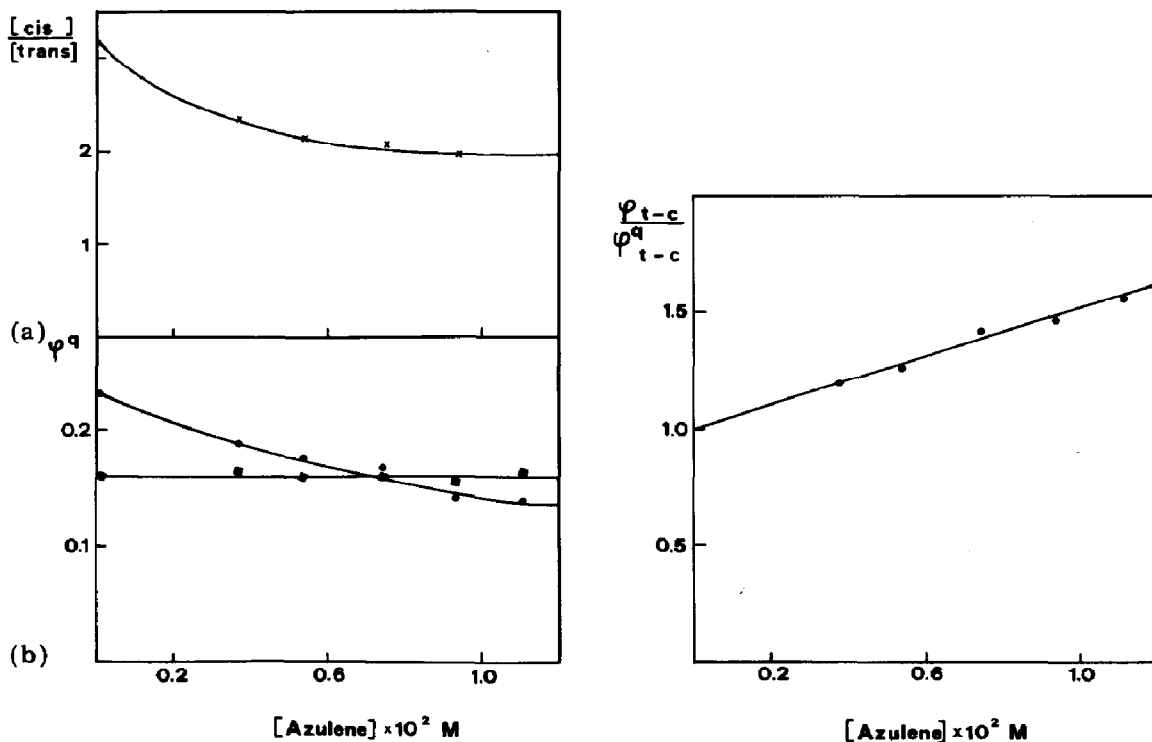


Fig. 1. Effect of azulene concentration on (a) the [cis]-to-[trans] ratio and (b) the quantum yields φ_{t-c}^a (●) and φ_{c-t}^a (■) in the direct photoisomerization of STP.

Fig. 2. Dependence of the $\varphi_{t-c}/\varphi_{t-c}^a$ ratio on the azulene concentration.

quencher concentration; the values of the extrapolated intercept and the slope are respectively 2 and 1460. A plot of the Φ_{c-t}/Φ_{c-t}^a ratio *versus* the concentration of azulene was a straight line with an extrapolated intercept of 2.6 and a slope equal to 0 (Fig. 3).

The classical mechanism for the sensitized photoisomerization under limiting quantum yield conditions and in the presence of azulene can be described by the following scheme of reactions:



where S and Q are respectively benzil and azulene, STP is the substrate in the initial form (*trans* or *cis*), STP' is the isomerized form (*cis* or *trans*) and p is a distorted state of intermediate configuration between the two

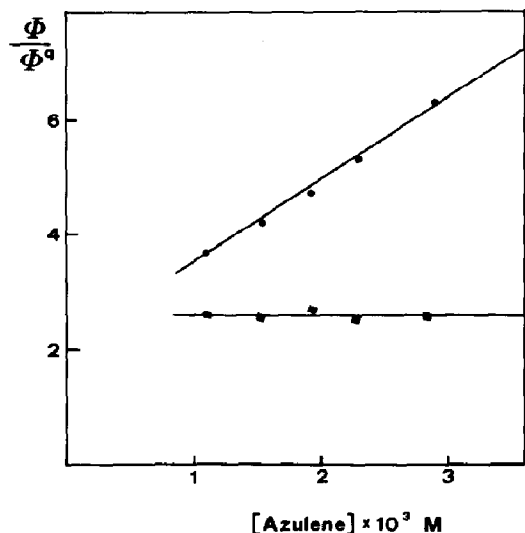


Fig. 3. Dependence of the Φ/Φ^0 ratio on the azulene concentration: ●, Φ_{t-c}/Φ_{t-c}^0 ; ■, Φ_{c-t}/Φ_{c-t}^0 .

isomers. The two processes ${}^3S \rightarrow S$ and ${}^3STP \rightarrow STP$ are not taken into account, the first because we work under conditions of limiting quantum yields and the second because $\Sigma\Phi = 1$.

In the above scheme of reactions the initial quantum yield $\Phi(\text{trans} \rightarrow \text{cis})$ or $\Phi(\text{cis} \rightarrow \text{trans})$ in the absence of quencher is given by

$$\Phi = \eta_{isc}(1 - \alpha)$$

and in the presence of quencher [6, 7]

$$\Phi^0 = \eta_{isc} \frac{k_2[STP]}{k_2[STP] + k_3[Q]} \frac{k_4}{k_4 + k_5[Q]} (1 - \alpha)$$

Consequently

$$\frac{\Phi}{\Phi^0} = \frac{k_2[STP] + k_3[Q]}{k_2[STP]} \frac{k_4 + k_5[Q]}{k_4}$$

By rearrangement we obtain

$$\frac{\Phi}{\Phi^0} = \left(1 + \frac{k_3[Q]}{k_2[STP]}\right) (1 + k_5\tau'[Q]) \quad (7)$$

where the first term represents the reciprocal of the energy transfer fraction by benzil to STP and τ' ($= 1/k_4$) is the lifetime of the quenchable state.

Under our experimental conditions the ratio $[Q]/[STP]$ was constant and equal to unity; consequently

$$1 + \frac{k_3[Q]}{k_2[STP]} = K'$$

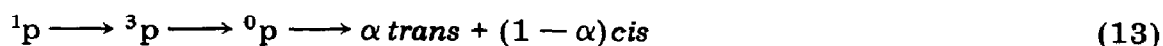
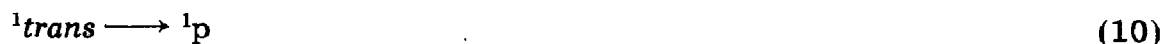
Relation (7) becomes

$$\frac{\Phi}{\Phi^q} = K' + K'k_5\tau'[Q] \quad (8)$$

The intercept of the plot of Φ/Φ^q versus $[Q]$ yields the value of K' and the ratio of the slope to the intercept yields the value of $k_5\tau'$. As shown in Fig. 3, the ratios Φ_{t-c}/Φ_{t-c}^q and Φ_{c-t}/Φ_{c-t}^q are both linear functions of $[Q]$ and therefore follow the relationship (8); from these plots the values of K' and $k_5\tau'$ for the *trans* and *cis* isomer can be obtained. We found that the K' values are 2 for the *trans* isomer and 2.6 for the *cis* isomer, i.e. both are good acceptors, as is azulene, accepting about 50% or more of the energy transferred by the sensitizer; the value of $k_5\tau'$ is 730 M^{-1} for the *trans* isomer and about zero for the *cis* isomer. These findings indicate that azulene quenches the $^3\text{trans}$ state whose lifetime is about $7 \times 10^{-7} \text{ s}$, given that $k_5 \approx 10^9$, whereas the ^3cis state is not quenchable because the value of τ' or k_5 is too small. No equilibrium $^3\text{trans} \rightleftharpoons ^3\text{p}$ can exist, because in this case Φ_{c-t}^q would increase as a function of the azulene concentration. The calculated value of the lifetime of the quenchable state $^3\text{trans}$ was consistent with the observation that this state exhibited phosphorescence at 77 K [1]. It should be mentioned that the observed effect of azulene on the photoisomerization of STP is analogous to that found for PTA.

If the same $^3\text{trans}$ state were implied in the pathway of the direct photoisomerization, i.e. if the intersystem crossing $^1\text{trans} \rightarrow ^3\text{trans}$ were efficient at ambient temperature, we should have found that $k_q\tau = k_5\tau'$. This is not the case because $k_q\tau \ll k_5\tau'$.

A reaction mechanism in agreement with the results found in direct irradiation is the following:



In this interpretation the state quenched by azulene in direct photoisomerization is the singlet $^1\text{trans}$ for which a lifetime of about $5 \times 10^{-8} \text{ s}$ is obtained. This lifetime is long enough for a singlet state and this finding is supported by the fact that fluorescence was observed [1]. Unfortunately process (12) cannot be experimentally verified; in fact, because of an overlap of the donor and acceptor fluorescences, it is not possible to carry out quenching experiments of STP fluorescence using azulene.

In the proposed mechanism the two processes, sensitized and direct, have the common precursor ^3p , attainable from the $^3\text{trans}$ or ^1p state, and in this sense the results are in agreement with the previous conclusions [1].

An alternative interpretation of the results of direct photoisomerization could be to attribute the difference between $k_q\tau$ and $k_5\tau'$ to the hypothesis that the direct photoisomerization can occur through a mixed singlet-triplet mechanism:



where only the ${}^3\text{trans}$ state was quenchable by azulene. However, we think that the first interpretation fits our experimental results better.

Finally, it is worth noting that the results are close to those found for stilbene and the group of analogues with substituents that do not influence the intersystem crossing [8]; however, for STP the crossing of the singlet and triplet pathways, which is excluded in the stilbenes, is probable.

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