

Styrene triplets: Absorption spectra, lifetimes and quantum yields

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Abstract

The triplet states of styrene, *p*-methyl-, *p*-methoxy- and *p*-chlorostyrene produced by direct excitation (266 nm) or by sensitization with triplet benzophenone in cyclohexane solution, were identified and their absorption spectra and their reactivity with triplet quenchers were determined. The absorption spectra are characterized by a band at about 280 nm (ϵ in the range 14000–24000 M⁻¹ cm⁻¹) and a weaker band (or shoulder) at about 320 nm ($\epsilon \approx 5000$ M⁻¹ cm⁻¹). For direct excitation, the quantum yields for triplet formation are 0.2–0.5. The rate constants for reaction of the triplets with O₂, 1,3-cyclohexadiene or ferrocene are of the order of 10⁹ M⁻¹ s⁻¹.

Keywords: Styrene triplets; Absorption spectra; Lifetimes; Quantum yields

1. Introduction

When the biphotonic ionization ($\lambda_{\text{excitation}} = 248$ and 266 nm) of a series of substituted styrenes was studied in polar solvents (water–alcohol mixtures), in addition to solvated electrons, the olefin radical cations and their subsequent reaction products, a rapidly decaying signal with λ_{max} in the range 270–290 nm was observed [1]. This signal was also present in non-polar solvents such as cyclohexane, where there was no evidence for photoionization.

In the case of styrene itself, a transient absorbing at 325 nm or less has previously been reported and assigned to the triplet [2,3]. However, the strong fluorescence of styrene in the spectral range between 300 and 330 nm [3,4] made the characterization of this signal difficult and therefore the assignment was only tentative.

The energy levels of the lowest excited singlet and triplet states of styrenes carrying aliphatic or aromatic substituents at the exocyclic double bond have been determined by optical perturbation spectroscopy using oxygen under a high pressure [5–7]. Furthermore, the quantum efficiency for intersystem crossing from S₁ to the lowest triplet state (T₁) and the triplet quenching rate constants for the reaction with, for example, oxygen and nitrogen oxide are known [3,8]. The triplet states of styrenes not substituted at the alkene bond were interpreted as perpendicular triplets, i.e. twisted at the alkene π orbitals by 90°. The chemical consequence of this geometry is the dominance of a biradical rather than a typical triplet character. On the basis of a biradical character the rapid

relaxation of and isomerization from the triplet states of these molecules can be more easily explained [9]. The pronounced tendency of the *p*-acetylstyrene triplet to add styrene [10] is in agreement with this picture.

In order to identify further the reaction channels leading to and following photoexcitation and photoionization, we have now taken another look at the excited states of various styrenes. With the commercial availability of high power lasers emitting in the UV range, it becomes important to distinguish between monophotonic and biphotonic photochemical processes. This is of particular relevance in the case of aromatics such as styrenes, which have an ionization threshold that can be reached by (consecutive) two-photon absorption (see for example [1,11,12]).

2. Experimental details

Direct excitation of the styrenes was performed with 3 ns pulses of 266 nm light (fourth harmonic from a Spectra Physics GCR-11 Nd-doped yttrium aluminium garnet laser; 1–10 mJ pulse⁻¹); the sensitization experiments with benzophenone were carried out with 355 nm light (third harmonic; 3 ns; 5 mJ). The analysing light (from a pulsed Osram XBO 450 lamp) was focused onto the sample cell and from there into the entrance slit of the monochromator. The overall time resolution of the equipment was 3 ns. Details of the apparatus have been described in [1].

The styrenes (*p*-H, *p*-Me, *p*-MeO and *p*-Cl) and 2-propenol (UV grade) were used as received (Aldrich). Water

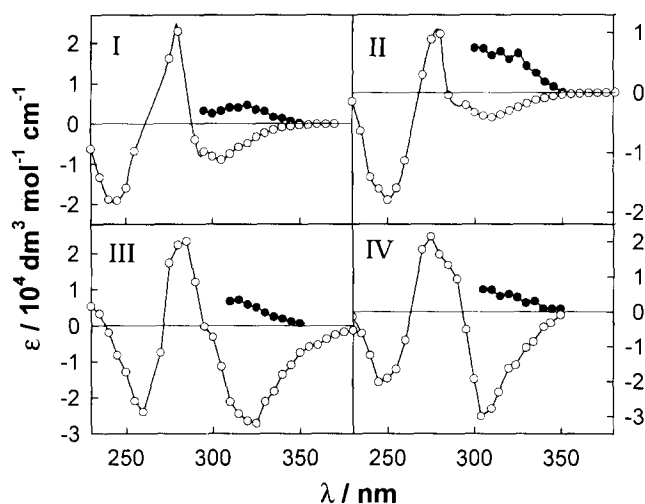


Fig. 1. Spectra of transients produced on photolysis of the styrenes I–IV as recorded 10 ns after the 266 nm pulse (○). For comparison, spectra are shown obtained via benzophenone sensitization, as monitored at 20 ns after the 355 nm laser pulse (●).

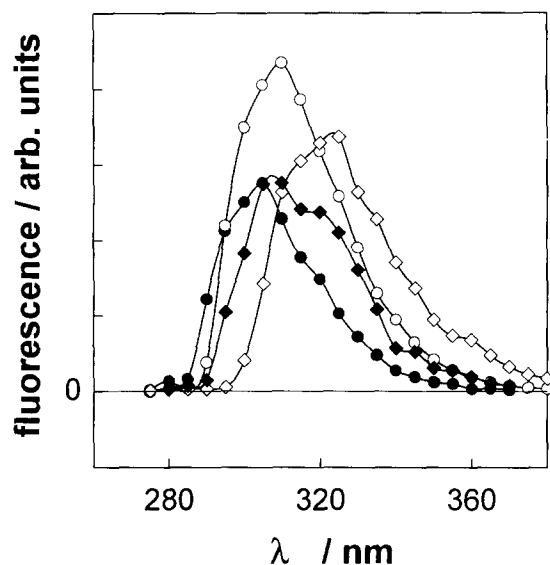


Fig. 2. Fluorescence spectra recorded 10 ns after the 266 nm laser pulse. The N_2 -bubbled cyclohexane solutions contained 1 mM I (●), 1 mM II (○), 0.2 mM III (◇) or 0.18 mM IV (◆).

Table 1

Lifetimes, emission and absorption maxima and extinction coefficients of the electronically excited styrenes M, measured in cyclohexane at room temperature

M	S_1		T_1				
	τ (ns)	λ_{max} (nm)	Direct excitation			Benzophenone sensitization	
			τ (ns)	ϕ	$\epsilon(275 \text{ nm})$ ($\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	τ (ns)	$\epsilon(320 \text{ nm})$ ($\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)
I	13 ± 1.5	305	24 ± 1.5	0.5 ± 0.1	13000 ± 5000	22 ± 3	4700
I	13.9^a	—	25^a	0.395^a	—	—	2200^a
II	10 ± 1	310	27 ± 1	0.4 ± 0.1	10000 ± 1500	21 ± 4	5500
III	6 ± 1	320	27 ± 1	0.2 ± 0.1	13000 ± 1500	25 ± 4	5800
IV	≤ 3	310	30 ± 1.5	0.4 ± 0.1	23000 ± 500	28 ± 2	5100

^a From [2], measured at 325 nm.

was doubly distilled and then purified with a Millipore Milli-Q Plus system. Cyclohexane (Merck, HPLC grade) was dried using a column filled with molecular sieves A4 and X13 (Zeosorb) and distilled. Benzophenone was recrystallized from ethanol; 1,3-cyclohexadiene was vacuum distilled.

3. Results and discussion

The styrenes investigated in this study (styrene (I), *p*-methylstyrene (II), *p*-methoxystyrene (III) and *p*-chlorostyrene (IV)) differ in the *p* substituent in the aromatic ring. On photolysis of 0.1–1 mM solutions of I–IV in cyclohexane with 266 nm laser pulses, negative signals between 300 and 350 nm (i.e. emission; see later), positive signals between 270 and 300 nm (i.e. absorption) and again negative signals (i.e. depletion of parent compound) below 270 nm were observed (Fig. 1, open circles).

The loss of absorption below 270 nm is caused by depletion of the parent styrenes which have a strong absorption band here, whereas the (short-lived) negative signal between 300 and 380 nm is due to the styrene fluorescence. In Fig. 2 are presented the fluorescence spectra corresponding to the styrene $S_0 \leftarrow S_1$ transition and in Table 1 are listed the emission maxima and the lifetimes of the S_1 states. As seen from Table 1, the fluorescence maxima (between $\lambda = 290$ nm and $\lambda = 350$ nm) and the fluorescence lifetimes do not depend very strongly on the nature of the *p* substituent.

In the region 290–380 nm, within 30 ns after the pulse the fluorescence emission is so intense that it overcompensates any absorption signal that may be present. However, in the range 275–285 nm the signals seen (see Fig. 1) are interpretable in terms of triplet–triplet absorptions. This assignment is based on the relatively long lifetimes of the species (see Table 1) and on the fact that they can be scavenged by typical triplet quenchers such as O_2 ($k(\text{IV}(T_1 + O_2)) = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$), 1,3-cyclohexadiene ($k = 5 \times 10^9$), and ferrocene ($k = 5.2 \times 10^9$). The yields of the styrene triplets were proportional to the absorbed laser power. It was found that, after decay of the triplet, at all wavelengths the absorptions returned to the values present before the pulse. This means that no (irreversible) photochemistry has taken

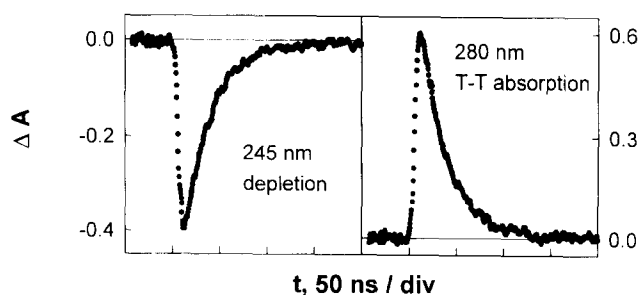


Fig. 3. Time profiles of the depletion and regeneration of styrene **IV** (at 245 nm) as a result of its triplet's decay (at 280 nm) recorded in a deaerated 0.2 mM solution of **IV** in cyclohexane.

place, i.e. the triplet relaxes to the singlet ground state without chemical consequence:

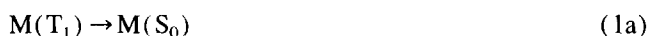
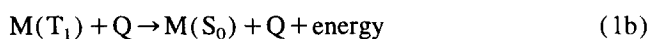


Fig. 3 contains a comparison of the time profile of regeneration of styrene **IV** at 245 nm with that of the decay of the styrene triplet at 280 nm. The traces are mirror images of each other. If a quencher **Q** is present, the lifetime of the triplet is reduced, owing to the reaction.



In contrast, in aqueous or alcoholic solution, from the analogous time profiles it is obvious that an only partial regeneration of the parent styrene absorption (250 nm) after the corresponding triplet decay (275 nm) takes place. In the region of styrene absorption, permanent consumption is visible and, in the absorption region of the triplet, a longer-lived transient is formed. This is demonstrated in Fig. 4 (analogous observations were made in the case of **IV** [1]). Both these effects – permanent styrene consumption and formation of a (transient) product – correspond to one another and can be explained in terms of the biphotonic formation of ionization products of the styrenes:



In alcoholic or aqueous solution, the radical cations are not directly observable (except for the case of *p*-methoxystyrenes); only their reaction products with nucleophiles are seen, i.e. benzyl-type radicals such as [1,11].

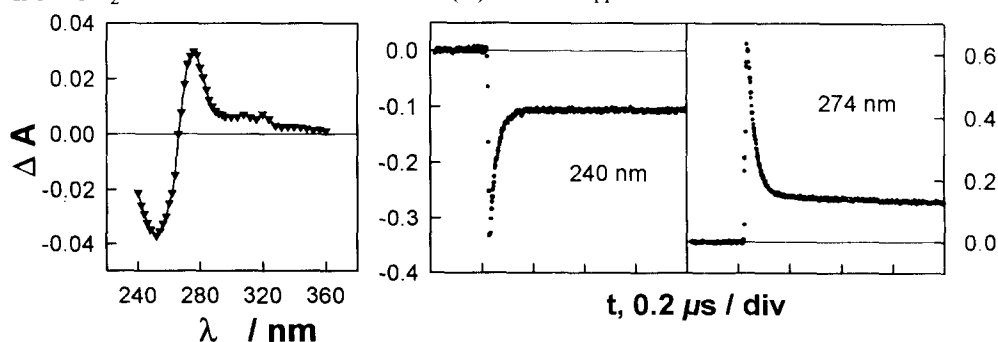
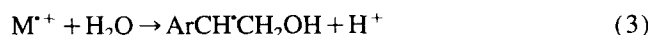


Fig. 4. 0.2 mM **II** in water containing 20% (v/v) of isopropanol and 1 (v/v) of dichloromethane. The spectrum was recorded 300 ns after the pulse, i.e. after decay of the triplet.

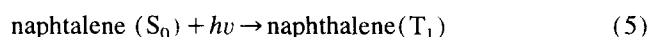
This is demonstrated for the case of **II** by the spectrum presented in Fig. 4. The benzyl-type radical is recognizable by the characteristic absorption at about 260 nm.

Concerning the situation in non-polar solvents such as cyclohexane, the information on absorption maxima, lifetimes and extinction coefficients of the triplets is summarized in Table 1. The lifetimes were obtained from single-exponential fits of the experimental absorption–time profiles at 280 nm (using excitation at 266 nm). The ϵ values were calculated on the basis of the observed depletion of the absorption of the parent styrenes at 245–260 nm and assuming that the triplets do not absorb at these wavelengths¹

In order to determine the quantum yields for triplet formation, the following photoreactions were used for actinometry:



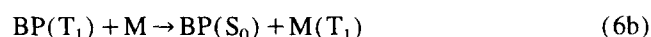
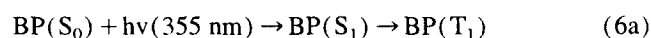
taking $\phi = 0.29$ [13], $\epsilon(e_{\text{aq}}^-/578 \text{ nm}) = 10\,600 \text{ M}^{-1} \text{ cm}^{-1}$ and



taking $\phi = 0.8$ [14], $\epsilon(\text{naphthalene}(T_1)/415 \text{ nm}) = 24\,500 \text{ M}^{-1} \text{ cm}^{-1}$.

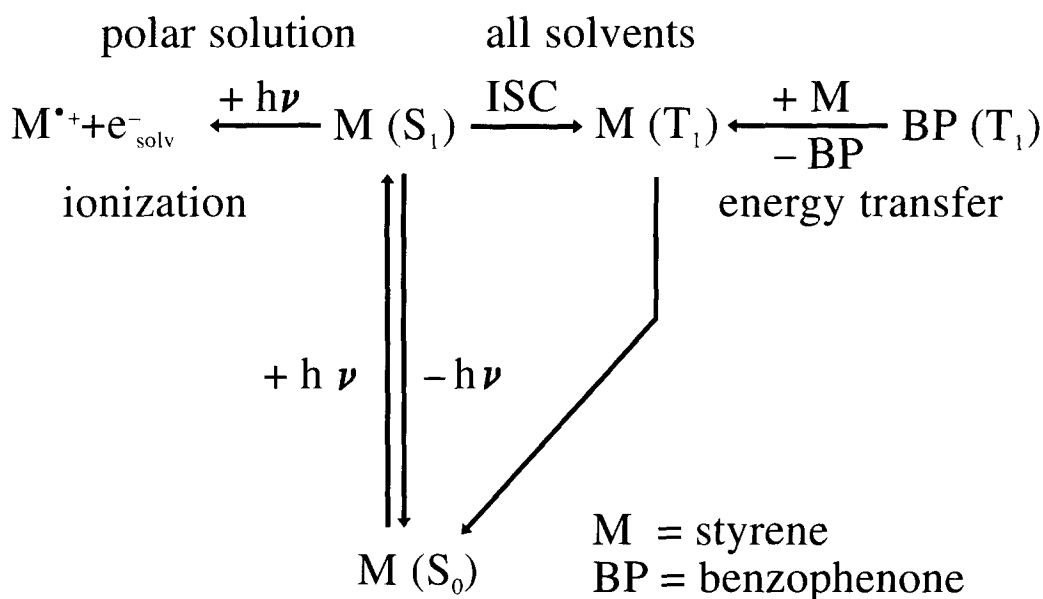
The quantum yields ϕ thus obtained (see Table 1) on the basis of reactions (4) and (5) and using the ϵ values measured as described above were found to be equal within the experimental error of $\pm 20\%$. The value obtained for styrene (**I**) is 0.5 ± 0.1 , which is in agreement with that (0.4) measured previously and 325 nm [2,3].

In order to circumvent the interference caused by the intense styrene fluorescence, the styrene triplets were also generated by sensitization of the parent compounds with benzophenone (BP):



Reaction (6b) was expected to be rapid because the difference of the T_1 energy levels of the reaction partners is as high as 28 kJ mol^{-1} [15]. In fact, by monitoring the effect

¹ It is likely that the absorption band of the triplet with $\lambda_{\text{max}} \approx 280 \text{ nm}$ extends into the region 245–260 nm. If this is the case, the $\epsilon(\text{triplet})$ values are upper limits.



Scheme 1.

on the BP(T₁) decay rate of different concentrations of styrenes, the rate constant for reaction (6b) was determined to be $3.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for **I**, which compares well with the previously determined values: 2.2×10^9 for α -methylstyrene, and 2.3×10^9 for 1,1-diphenylethylene [4,16]. These values are close to the diffusion limit in cyclohexane.

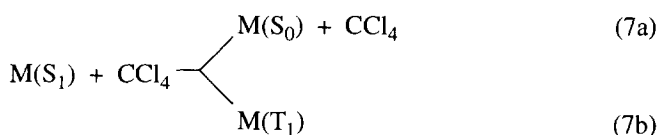
With 0.1 M styrene as scavenger of the triplet of benzophenone, the transfer (reaction (6b)) thus takes place within a few nanoseconds and, after this time, the resulting styrene triplet absorption is observed (see Fig. 1, full circles). In the case of styrene, the ϵ value thus determined at 320 nm is $4700 \text{ M}^{-1} \text{ cm}^{-1}$, which compares with $2200 \text{ M}^{-1} \text{ cm}^{-1}$ as measured directly [2]. It is thus evident that the styrene triplets have two absorption bands: one at about 280 nm and the other at about 320 nm. It is evident from Table 1 that the lifetimes of the triplets are independent of their generation (direct vs. indirect). This shows that the bands at 280 and 320 nm represent the same chemical species.

The styrene triplets were characterized by their reactivity with the quenchers oxygen, 1,3-cyclohexadiene and ferrocene. The rate constants determined from the (linear) dependences of the rates of triplet decay (measured at 280 nm) on the concentrations of the quenchers are 1×10^{10} , 5×10^9 and $5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

The triplet formation described proceeds in non-polar as well as in polar solution. In polar solution, however, a second photon can promote an electron from the M(S₁) state to the ionization continuum (see scheme below). That this is possible is probably due to the efficient 'undelayed' solvation of the ionization products, i.e. e⁻ and M^{•+}, as a result of which a solvation energy of about 3.5 eV becomes available to stabilize the transition state for ionization. With photon densities above a few millijoules per pulse of the 266 nm laser light, the biphotonic ionization becomes the dominating process, superimposing completely the monophotonic channel.

This is recognizable from Fig. 4, in which both reaction channels are demonstrated; the spikes in the time profiles as caused by M(T₁) and the longer-lived species are representative of ionization products. The spectra of the latter are also contained in Fig. 4, left-hand part, in this case showing the absorption spectrum of the hydroxymethyl-substituted benzyl radical of **II**, i.e. *p*-Me-C₆H₄-C[•]HCH₂OH. As already mentioned, in polar media only in the case of *p*-methoxystyrenes (**III** and analogous compounds) the radical cations M^{•+} are sufficiently long lived to be visible in the nanosecond time range [1,11] (Scheme 1).

As an additional reactant, CCl₄ was studied. In the presence of CCl₄, the initial yields and the lifetimes of the triplets M(T₁) were found to be decreased and new transients were observed to be present (for **IV**, see Fig. 5 for time profiles; lifetime of transient 3–4 μs) (for **I–IV**, the absorption spectra of the transients produced are shown in Fig. 6). This reduction is suggested to be due to quenching of the singlet state according to reaction (7a)



In fact, from the dependence on concentration of CCl₄ of the rate of fluorescence decay as monitored at 300 nm, the rate constant for quenching of the styrene excited singlet state by CCl₄ was measured to be $4.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Since the quenching of the fluorescence resulted in only a partial disappearance of the triplet as measured at about 280 nm, the triplet must also be a product of the reaction of M(S₁) with CCl₄. Therefore it is necessary to assume that, in competition with the physical quenching reaction (7a), a CCl₄-induced intersystem crossing takes place (reaction (7b)), a process

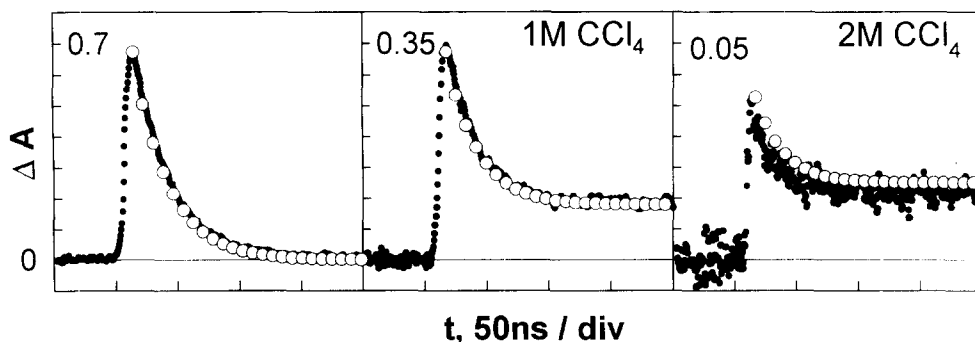


Fig. 5. Effect of addition of carbon tetrachloride on the time profile of the absorption at 280 nm on photolysis of a 0.2 mM solution IV in *c*-hexane: O, from a computer fit of the decay curves based on first-order kinetics.

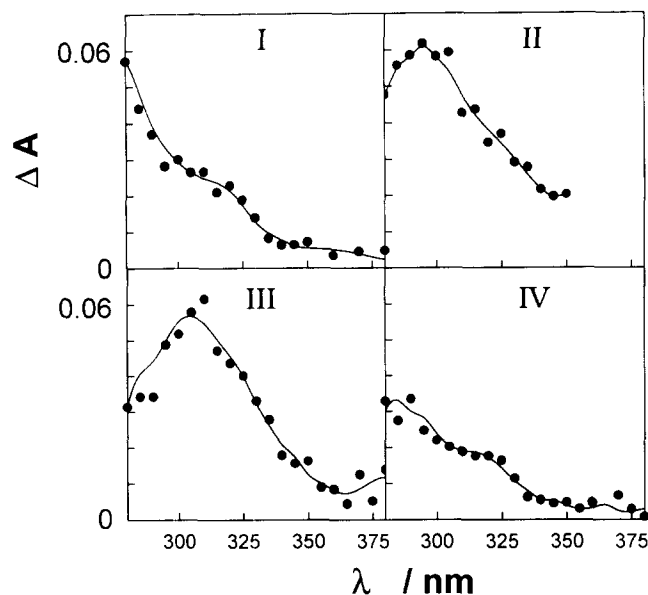


Fig. 6. Absorption spectra of the transient products of the quenching of excited styrenes with 2 M carbon tetrachloride in deaerated cyclohexane solution, recorded 300 ns after the laser pulse: 2.4 mM of I, 0.7 mM of II, 0.3 mM of III and 0.5 mM of IV.

made possible by the 'heavy-atom' effect of the four Cl atoms in CCl_4 .

From the dependence on $[\text{CCl}_4]$ of the lifetime of the triplet of styrene (monitored at 280 nm), the rate constant for its reaction with carbon tetrachloride (reaction (8)) is estimated to be about $5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. The transients formed by quenching of the excited styrenes with CCl_4 were found to react rapidly with O_2 ($k = (1-2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). On this basis, the transients are identified as radicals, probably the Cl-atom adducts of the styrenes, formed according to

$$\text{M}(\text{T}_1) + \text{CCl}_4 \rightarrow \text{M} - \text{Cl} + \text{CCl}_3 \quad (8)$$

With CCl_4 , homolytic breaking of one of the C–Cl bonds upon energy transfer from electronically excited aromatics is a well-known phenomenon (see, for example [17]).

4. Summary and conclusions

The direct excitation ($\lambda = 266 \text{ nm}$) of styrene and several *p*-substituted derivatives of styrene in polar solvents results

in the formation of ionic species (solvated electrons and radical cations or their subsequent products). In addition, electronically excited states are observable by their strong fluorescence and short-lived absorptions. In non-polar solvents, ionization processes are not observed. The absorptions detected could be assigned to the triplet states of the styrenes. The triplets were characterized by quenching and energy transfer experiments, and the quantum yields and molar extinction coefficients determined.

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