Photolysis of *trans-α,α'*-dihalostilbenes ☆

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Abstract

The photochemical behaviour of trans isomers of the four α,α'-di-X-stilbenes ($X \equiv F$, Cl, Br or I in the olefinic positions) was studied in solution at room temperature. The main photoreaction of F_2- or Cl_2-stilbene is trans → cis isomerization, whereas diphenylacetylene (DPA) and X_2 are the photoproducts of Br_2- and I_2-stilbene. The quantum yields of Br_2 and I_2 elimination are typically 0.2 and 0.6 respectively and are essentially independent of the kind of solvent and the irradiation wavelength (222, 254 or 313 nm). The same transient ($\lambda_{max} \approx 410$ nm), observed by laser flash photolysis ($\lambda_{exc} = 248$ nm) of either Br_2- or I_2-stilbene, is assigned to the lowest triplet state of DPA which is formed by consecutive absorption of two photons; the first step generates DPA via the excited singlet state of *trans*-X_2-stilbene by homolytic cleavage of the two C—X bonds and subsequent excitation of DPA within the 20 ns laser pulse yields $^3DPA^*$ via intersystem crossing.

Keywords: Dihalostilbenes; Photoisomerization; Diphenylacetylene

1. Introduction

The cis ⇌ trans photoisomerization of stilbenes has been the subject of numerous investigations [1–11]. Its mechanism depends strongly on the nature and position of substituents on stilbene. While trans → cis photoisomerization of unsubstituted stilbene occurs via a singlet mechanism [1–3], bromine substitution at the 4 position gives rise to an additional pathway which is caused by a heavy-atom-enhanced intersystem crossing to an upper excited triplet state [7]. Generally the lowest triplet state of 1,2-diarylethylenes becomes detectable either in glassy media, where trans → cis photoisomerization is completely inhibited, or in fluid media after energy transfer from excited sensitizers, since its quantum yield of intersystem crossing is too low [11]. When stilbene is substituted by halogen atoms in olefinic positions, other photochemical processes may occur [4,5,12–14]. For α-X-monosubstituted stilbenes ($X \equiv Cl$, Br, I) cis- and trans-stilbene, diphenylacetylene (DPA) or phenanthrene have been reported as photoproducts, in contrast with fluoro substitution [4,12]. Related photoreactions of diarylvinyl bromides, involving radicals and/or ionic intermediates, have been reported [15–23].

Little is known about the photochemical properties of α,α'-dihalogenated stilbenes. For α,α'-difluorostilbene and α,α'-

dichlorostilbene (F_2- and Cl_2-stilbene) in solution at ambient temperature fluorescence is negligible and trans → cis photoisomerization is the main deactivation pathway with substantial quantum yield ($\Phi_{t \rightarrow c}$) [4]. In contrast, owing to strong sterical hindrance, no stable cis isomers could be isolated for α,α'-dibromostilbene and α,α'-diiodostilbene (Br_2- and I_2-stilbene) [13]. They are also examples of 1,2-diarylethylenes which are substituted by heavy atoms, but the role of the triplet state is not yet known.

In this work the primary photoproducts of *trans*-X_2-stilbenes in solvents of different polarity were studied by UV spectroscopy and gas chromatography (GC) and high performance liquid chromatography (HPLC) analyses. Intermediates involved in the relaxation pathway and in secondary photoreactions were detected by laser flash photolysis. Formation of DPA in substantial yield (Φ_{DPA}) was observed upon steady state irradiation of Br_2- and I_2-stilbene. While no X_2-stilbene triplet could be detected with a time resolution of 20 ns, the only observed transient is assigned to the lowest triplet of DPA. The mechanism of dehalogenation is discussed.

2. Experimental details

The *trans*-X_2-stilbenes ($X \equiv Cl$, Br, I) and *trans-α*-bromostilbene were prepared according to Refs. [4,13] and purified by sublimation (Cl_2-stilbene) or recrystallization;

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trans-F$_2$-stilbene was received from K and K Lab. and diphenylacetylene (DPA, tolane) from EGA. GC analysis of the four trans-stilbenes showed a purity of typically 99.8%. cis-1,3-Pentadiene (EGA) was purified by distillation, DPA was zone refined (99%) and ferrocene (Merck) was recrystallized. The molar absorption coefficients of DPA are $\epsilon_{295} = 2.9 \times 10^4$ M^{-1} cm^{-1} and $\epsilon_{278} = 3.4 \times 10^4$ M^{-1} cm^{-1}. The solvents (Merck) were of the purest optical quality commercially available (e.g. acetonitrile: Uvasol quality) or further purified by distillation (e.g. methylcyclohexane (MCH), cyclohexane, dioxane and methanol).

Steady state irradiation measurements were carried out using a 1000 W mercury–xenon lamp and a monochromator (Schoeffel, bandwidth 7 nm) for $\lambda_{irr} = 313$ nm, a low pressure mercury lamp for $\lambda_{irr} = 254$ nm [7–9] and a KrCl excimer lamp (Lichttechnisches Institut der Universität Karlsruhe) for $\lambda_{irr} = 222$ nm. Absorption spectra were recorded on a spectrophotometer (Perkin–Elmer 554). The incident light intensity was measured by a ferrioxalate actinometer [24]. In addition, photohydrate formation from uridine was used for $\lambda_{irr} = 222$ and 254 nm, $\Phi = 0.018$, as a second standard [25].

For laser excitation the 248 nm line of an excimer laser (Lambda Physik, EMG201 MSC, incident pulse energy $E_L \leqslant 100$ mJ) was used [26]. Conventional flash photolysis was only applied for determination of the lifetime of ^{3}DPA* under conditions of inefficient quenching (T–T annihilation and self-quenching). For sensitized measurements the third harmonic of a neodymium laser (J.K. Lasers, $E_L \leqslant 20$ mJ, $\lambda_{exc} = 353$ nm) was also used. The detection system and the experimental set-up (1 cm path length) were as described elsewhere [9,26]. To prevent formation of DPA by irradiation with the analysing xenon lamp (pulse width 1–2 ms), a cut-off filter (Schott, GG 350) was placed in front of the cell. Conversions of 10% DPA could be achieved from I$_2$-stilbene by one 248 nm laser pulse and therefore laser excitation of X$_2$-stilbene was carried out with fresh solutions in a flow cell. For I$_2$-stilbene the possibility of dissociation into DPA and iodine has been reported [13], but control measurements showed that it remained stable (e.g. for 10 min) in MCH even at 90 °C. Unless otherwise indicated, the experiments were carried out at room temperature and the samples were purged with argon.

3. Results

3.1. Photoproducts and quantum yields

Irradiation at 254 nm of trans-Br$_2$-stilbene (0.1 mM) in cyclohexane results in a new absorption spectrum with characteristic maxima at 275 and 293 nm (Fig. 1a). From UV and GC analyses the prevailing photoproduct was identified as DPA. Substantial conversions (up to 90%) of Br$_2$-stilbene to DPA were determined by both methods. Photochemical formation of DPA and decomposition of Br$_2$-stilbene are

shown in Fig. 2 as a function of the incident light fluence. DPA as major product absorbing in the 200–300 nm range was also observed with Br$_2$-stilbene in more polar solvents, e.g. acetonitrile or alcohols. Keeping the conversion below 20%, no indication was found by GC analysis for other possible photoproducts such as trans- and cis-stilbene, phenanthrene, trans-α-bromostilbene or 1,2-dibromo-1,2-diphenylethane. The latter is in contrast with Ref. [14], where photochemical formation of 1,2-dibromo-1,2-diphenylethane from trans-Br$_2$-stilbene in cyclohexane or benzene has been reported.
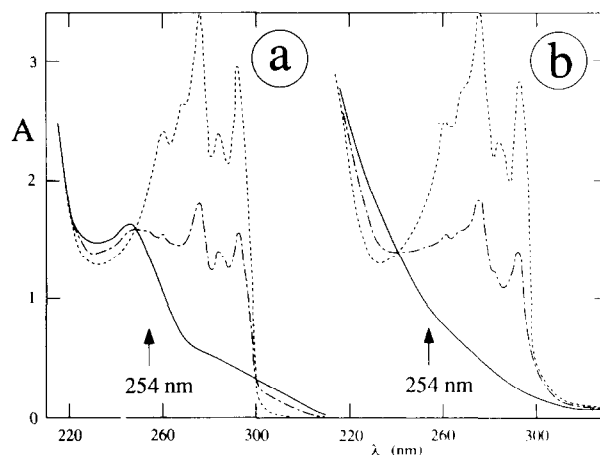

Fig. 1. Absorption spectra before (full lines) and after irradiation at 254 nm (broken lines) of (a) trans-Br$_2$-stilbene in cyclohexane and (b) trans-I$_2$-stilbene in acetonitrile.
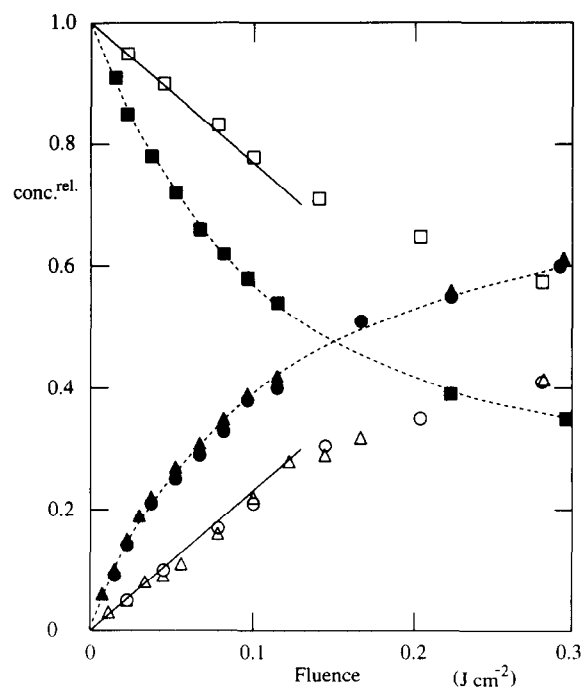

Fig. 2. Photolysis at 254 nm of trans-Br$_2$-stilbene in argon-saturated cyclohexane (open symbols) and trans-I$_2$-stilbene in acetonitrile (full symbols); relative concentrations of X$_2$-stilbene (squares) and DPA (circles) from GC and conversion (triangles) from UV spectra.

Table 1

Quantum yield of formation of DPA from trans-Br₂- and trans-I₂-stilbene [a]

Solvent	λ_{irr} (nm)	Φ_{DPA}	
		Br	I
Cyclohexane	254	0.20 [0.29] [b]	0.55 [0.83]
	313	0.18	0.53
	222	0.21	0.55
Dioxane	254	0.18	0.49
Dioxane + H₂O	254	0.15	0.38
tert-Butanol	254	0.19 (0.12) [c]	0.69 (0.4)
2-Propanol	254	0.16 (0.10)	0.63 (0.4)
Methanol	254	0.24 (0.14)	0.70 (0.4)
	222	0.2	0.65
Methanol + H₂O	254	0.18	0.55
Acetonitrile	254	0.19 (0.16)	0.68 (0.55)
	313	0.18	0.63
	222	0.21	0.64
Acetonitrile + H₂O	254	0.15	0.52

[a] At 25 °C in argon-saturated solution; amount of water, 25% (vol).
[b] Values in brackets: at 90 °C.
[c] Values in parentheses: in O₂-saturated solution.

Similar photochemical changes in the UV spectra were observed for trans-I₂-stilbene; an example is shown in Fig. b. Formation of I₂ in cyclohexane is indicated by a comparison of irradiated I₂-stilbene with a non-irradiated solution of DPA and I₂, having a further absorption maximum at about 10 nm. A positive identification, however, is limited to non-polar media because of charge transfer (CT) bands in slightly and strongly polar solvents [27]. Examples of the photoconversion are shown in Fig. 2 for Br₂-stilbene in cyclohexane and I₂-stilbene in acetonitrile. The strong curvature in the plots of the concentrations vs. the fluence at 254 nm is mainly due to the absorption of DPA. Note that ϵ_{254} is significantly larger for DPA than for Br₂- and I₂-stilbene (Figs. 1a and 1b respectively). GC in various solvents or HPLC in polar media is in agreement with the UV analysis.

The quantum yield of formation of DPA was obtained from the initial linear part of log A_{295} vs. fluence for low conversion (10% or less). Φ_{DPA} at room temperature is large for I₂-stilbene in non-polar as well as polar solvents, e.g. cyclohexane vs. acetonitrile, and depends only slightly on the nature of the solvent (Table 1). The Φ_{DPA} values for Br₂-stilbene also show no medium-dependent specificity and are roughly one-third of the values for I₂-stilbene. The Φ_{DPA} values for both stilbenes were found to be independent of λ_{irr}, which was changed from 254 to either 313 or 222 nm. The presence of oxygen has no (or only a small) reducing effect on Φ_{DPA}. Increasing the temperature to 90 °C for I₂-stilbene in MCH gives rise to an approximately 50% increase, i.e. the maximum value found in this work is $\Phi_{DPA} = 0.8$. Decreasing the temperature to −110 °C for Br₂-stilbene in ethanol reduced Φ_{DPA} by a factor of approximately 10.

To further test for the nature and fate of the eliminated halogen species in polar media, water was added to dioxane, methanol or acetonitrile solution. The presence of water has some minor effects on the spectra of Br₂- and I₂-stilbene

before and during irradiation, but does not strongly influence the photochemical results. In particular, addition of approximately 14 M water to X₂-stilbene in dioxane, methanol or acetonitrile reduces Φ_{DPA} by 20%–40% (Table 1). With Br₂-stilbene, in contrast with I₂-stilbene, protons are formed, but this is ascribed to a secondary photoreaction, as the proton concentration for low conversion is negligible and becomes significant only upon prolonged irradiation.

With F₂-stilbene in several solvents, using either 313 or 254 nm, only trans → cis photoisomerization was observed as the primary process. The photochemical features are close to those of parent trans-stilbene. With Cl₂-stilbene trans → cis photoisomerization and formation of DPA in small amounts were observed using $\lambda_{irr} = 313$ or 254 nm. The Φ_{DPA} value in cyclohexane, methanol and acetonitrile is well below 0.01. However, several products other than cis-Cl₂-stilbene and DPA were also detected by GC in cyclohexane or methanol (they were not identified). For comparison, with $\lambda_{irr} = 313$ nm, $\Phi_{t \to c} = 0.35$ for F₂-stilbene and 0.41 for Cl₂-stilbene in a 2:1 mixture of isohexane and isopentane at room temperature have been reported [4].

3.2. Properties of the DPA triplet state

A transient with a maximum at 408 nm was observed for DPA in acetonitrile concomitant with the exciting 248 nm laser pulse (Fig. 3a). T–T absorption maxima of DPA in
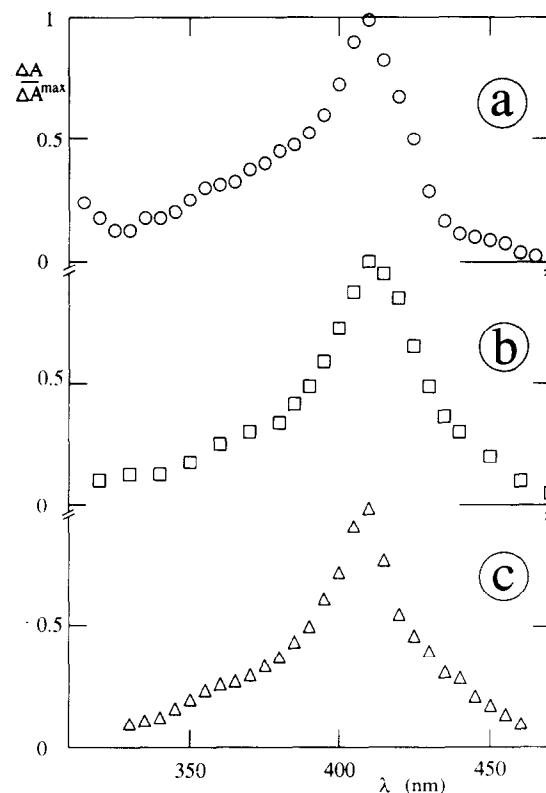

Fig. 3. Transient absorption spectra of (a) DPA in acetonitrile, (b) trans-Br₂-stilbene in cyclohexane and (c) trans-I₂-stilbene in acetonitrile (under argon), measured 100 ns after the 248 nm laser pulse.

Table 2

Absorption maximum and lifetime of the transient of DPA and *trans*-X$_2$-stilbenes and rate constants of quenching [a]

Compound	Solvent	λ_{max} (nm)	τ_T (μs)	k_{ox} (10^9 M^{-1} s^{-1})	k_q [b] (10^9 M^{-1} s^{-1})
DPA	Cyclohexane	405	10, 100 [c]	1.2	5 (4)
	Acetonitrile	408	20	1.5	7
	Methanol	410	80 [c]	1.3	8
	2-Propanol	409	15		
Br$_2$-stilbene	Cyclohexane	406	5		
	Acetonitrile	410	8	1.5	6 (5)
	2-Propanol	409	6		
I$_2$-stilbene	Acetonitrile	410	5	1.6	

[a] At 25 °C, in argon-saturated solutions, $\lambda_{exc} = 248$ nm unless indicated otherwise.

[b] For ferrocene; values in parentheses refer to *cis*-1,3-pentadiene as quencher.

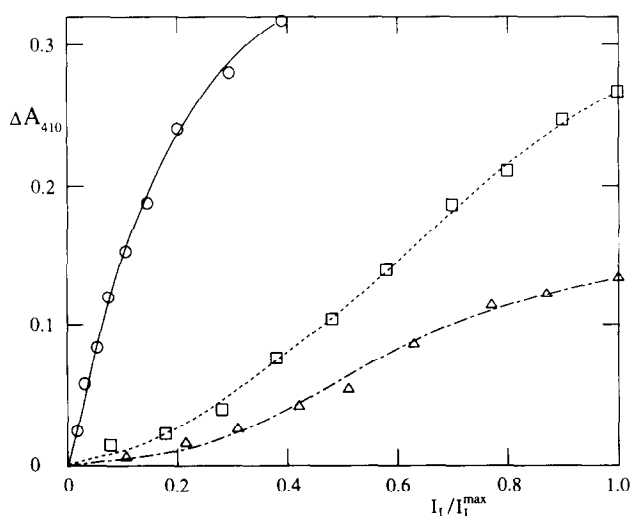[c] Obtained from conventional flash photolysis.

Fig. 4. Plots of the transient absorbance (after the laser pulse) at 410 nm vs. the incident laser intensity for DPA (○), *trans*-Br$_2$-stilbene (△) and *trans*-I$_2$-stilbene (□) in argon-saturated acetonitrile, $\lambda_{exc} = 248$ nm (flow-through cell).

glycerol at 418 and 308 nm have been reported [28]. The observed transient is assigned to the lowest triplet state (^{3}DPA*) on the basis of energy transfer measurements to DPA and from ^{3}DPA*. The triplet is quenched by low energy triplet quenchers such as 1,3-pentadiene or ferrocene (Q). From linear plots of the first-order decay rate constant (k_{obs}) vs. [Q], quenching rate constants $k_q = (4-8) \times 10^9$ M^{-1} s^{-1} were obtained (Table 2). The rate constants for quenching by oxygen, obtained from the triplet lifetimes ($\tau_T = k_{obs}^{-1}$) in argon-, air- and O$_2$-saturated solution, are significantly smaller, $k_{ox} = (1.2-1.5) \times 10^9$ M^{-1} s^{-1}.

The lifetime of ^{3}DPA* lies in the 80–100 μs range when carefully deoxygenated cyclohexane or methanol solutions are studied by conventional flash photolysis, where quenching effects virtually do not contribute (path length 15 cm). On excitation of DPA in acetonitrile by 248 nm laser pulses the triplet decay follows mixed first- and second-order kinetics. Owing to a smaller path length (1 cm), higher DPA concentrations were used for excitation by laser pulses and this gives rise to quenching by DPA in the ground state. The

rate constant for self-quenching was measured as about 1×10^8 M^{-1} s^{-1} in acetonitrile. In addition, strong T–T annihilation was found; a 10-fold increase in the incident laser intensity (I_L) caused a similar reduction in the first half-life. Therefore the lifetime obtained by laser flash photolysis represents only a lower limit for τ_T. A plot of the transient absorbance (ΔA_{410}) vs. I_L shows initially a linear dependence, reaching a saturation value as expected for a one-photon process (Fig. 4).

The same T–T absorption spectrum was observed (above 380 nm) after energy transfer from the triplet states of benzophenone ($E_T = 286$ kJ mol^{-1}) in benzene or xanthone ($E_T = 309$ kJ mol^{-1}) in acetonitrile using $\lambda_{exc} = 353$ nm. It is interesting to note that no remaining transient, in contrast with DPA, could be observed with Br$_2$- or I$_2$-stilbene under otherwise the same conditions, e.g. xanthone-sensitized excitation in acetonitrile. Energy transfer from the phenanthrene triplet ($E_T = 254$ kJ mol^{-1}) to DPA was unsuccessful, as the lifetime of the sensitizer is not discernibly reduced under comparable conditions, and no new transient around 410 nm was found. This is consistent with an energy of 261 kJ mol^{-1} for ^{3}DPA* [29].

3.3. Laser flash photolysis of trans-X$_2$-stilbenes

No transient could be detected with *trans*-F$_2$-stilbene and *trans*-Cl$_2$-stilbene in solution at room temperature at the end of the 248 nm pulse. This is consistent with a low quantum yield of intersystem crossing and $\Phi_{DPA} < 0.01$, in agreement with the singlet mechanism for trans → cis photoisomerization, as for parent stilbene [11]. Twisting about the C=C double bond in the excited singlet state ($^1S_t^* \rightarrow {}^1S_p^*$) is illustrated in Scheme 1 (left side); the stable isomers are formed by further twisting in the ground state.

A transient absorption spectrum with $\lambda_{max} = 410$ nm was observed on excitation of *trans*-Br$_2$-stilbene in cyclohexane (Fig. 3b). This transient (T$_{410}$) is formed during the laser pulse and decays essentially by first-order kinetics. Virtually the same transient spectrum and no discernible absorbance at wavelengths longer than about 500 nm were recorded for
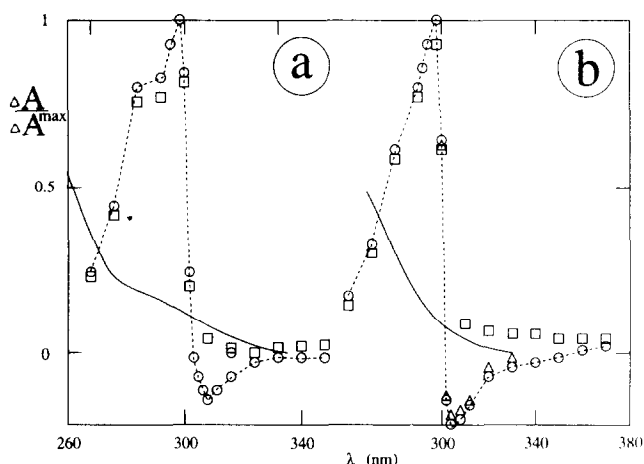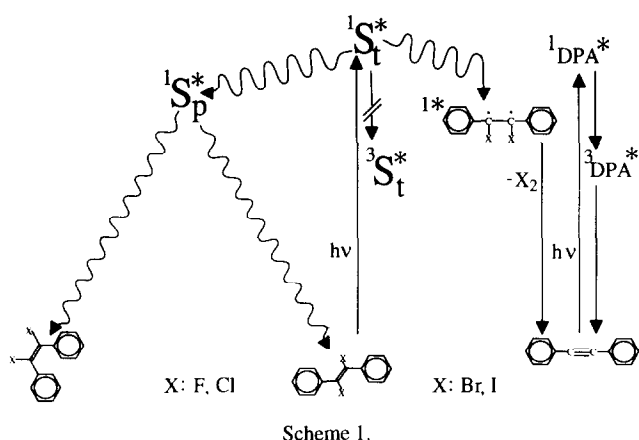
Scheme 1.

Fig. 5. Transient absorption spectra upon 248 nm pulse excitation of (a) *trans*-Br$_2$-stilbene and (b) *trans*-I$_2$-stilbene in argon-saturated cyclohexane after 0.2 μs (□), 2 μs (△) and 1 s (○); $\Delta A^{max} \approx 0.3$; full line, ground state absorption, $A_{248} = 1$.

trans-I$_2$-stilbene (Fig. 3c). T$_{410}$ is quenched by oxygen, ferrocene and 1,3-pentadiene at rates similar to those with ^{3}DPA* (Table 2).

On repeated flashing of Br$_2$- or I$_2$-stilbene, ΔA_{410} (just after the laser pulse) and the DPA concentration increase in a similar manner. It could be clearly demonstrated that T$_{410}$ is formed on excitation of fresh solutions of *trans*-X$_2$-stilbene in the absence of DPA (less than 0.1%). A sigmoidal dependence was observed for ΔA_{410} as a function of I_L (Fig. 4). At low I_L, ΔA_{410} follows a square dependence on the intensity, which changes to a nearly linear dependence at higher I_L, finally reaching a saturation value.

In order to study the kinetics of the photoreaction, nonpolar media were used, as in moderately and strongly polar solvents Br$_2$ and I$_2$ have CT bands in the range below 400 nm [27] (they may contribute at higher conversion owing to photoreactions of X$_2$). In agreement with the steady state spectra, an isosbestic point at 300 nm was observed for Br$_2$- and I$_2$-stilbene in cyclohexane upon pulsed excitation (Figs. 5(a) and 5(b)). The increase in ΔA below 300 nm and the decrease in ΔA between 305 and 380 nm, e.g. 1 s after the 248 nm pulse, are due to the photoconversion *trans*-X$_2$-stil-

bene → DPA and the absorption of Br$_2$ and I$_2$ can be neglected. The increase in ΔA at 260–300 nm, due to the formation of DPA, appears at the end of the laser pulse, whereas the bleaching is delayed. For I$_2$-stilbene the final bleaching is approached within 2 μs (Fig. 5(b)) and longer half-lives were found for Br$_2$-stilbene.

4. Discussion

4.1. Assignment of the transients

Photolysis of Br$_2$- or I$_2$-stilbene in cyclohexane or acetonitrile at room temperature yields DPA as the major absorbing photoproduct (Figs. 1 and 2). The environmental conditions, such as the nature of the solvent (e.g. polarity) and the presence or absence of oxygen or water, have only a small influence on the photoreaction (Table 1). This indicates short-lived intermediates and excludes involvement of a triplet state (unless the lifetime is unusually short). The question arises as to the nature of T$_{410}$ (Figs. 3(b) and 3(c)). Possible species are (1) a triplet state of X$_2$-stilbene, (2) the radical Ph—$^\cdot$C=CX—Ph, (3) the biradical Ph—$^\cdot$C—C$^\cdot$—Ph, (4) a radical cation, (5) a carbocation and (6) the triplet state of DPA.

(1) Assignment of T$_{410}$ to the lowest trans triplet state (^{3}S$_t$*) is excluded, since T$_{410}$ was not formed by energy transfer from a high energy triplet donor (e.g. xanthone or benzophenone). Triplet lifetimes below 100 ns rather than in the microsecond range have been reported for substituted *trans*-stilbenes in fluid solutions [6–9,11].

(2) If T$_{410}$ were the Ph—$^\cdot$C=CBr—Ph radical, it would be expected to abstract a hydrogen from the solvent, thereby forming *trans*-α-bromostilbene. However, α-bromostilbene was not detected by GC analysis of irradiated Br$_2$-stilbene even in solvents in which H atom abstraction is favoured (e.g. 2-propanol). It should be noted that the intermediacy of the radical Ph—$^\cdot$C=CBr—Ph has been proposed for the photolysis of *trans*-α-bromostilbene [12]. Corresponding radicals have been discussed in the photochemistry of 1,1-diarylvinyl bromides [19–23].

(3) If T$_{410}$ were the biradical, its lifetime would be long enough for H atom abstraction from the solvent. This effect should lead to a dependence of the transient lifetime on the solvent properties. However, similar lifetimes of T$_{410}$ were observed in solvents with different H donor properties (Table 2). Furthermore, H atom abstraction should result in formation of unsubstituted *trans*- and *cis*-stilbene, but no stilbene isomer was found by GC and UV analyses.

(4) Photoionization of X$_2$-stilbene in solution should initially yield a radical cation and the solvated electron (e_{solv}^-). Although the lifetime of e_{solv}^- decreases on going from water to methanol and further to less polar solvents, e_{solv}^- can be detected by our flash photolysis system, as was shown in other cases [26]. However, for Br$_2$- or I$_2$-stilbene in methanol no transient was observed between 600 and 800 nm, where

e_{solv}^- absorbs. Therefore T_{410} cannot be a radical cation or a resulting neutral radical. If a radical cation were to originate from electron transfer from atomic X to the corresponding radical, rapid formation of $X_2^{\cdot-}$ with maxima at about 370 and 710 nm would be expected [30]. However, this species could not be detected either for Br_2- or I_2-stilbene in methanol or mixtures with water (25%). For comparison, $I_2^{\cdot-}$ was clearly observed 0.1 μs after the 248 nm pulse using KI in methanol ($A_{248} = 0.5$–2 cm^{-1}).

(5) A precedence for photoheterolysis of a vinyl halide, besides photohomolysis yielding vinyl radicals, is given by 1-(p-R-phenyl)-2-(2,2'-biphenyldiyl)vinyl halides with $R \equiv CH_3$ or OCH_3 [23]; in fact, for the bromides it has been shown recently that a transient with $\lambda_{max} = 340$ and 355 nm respectively is the vinyl cation. Decay of the vinyl cation is not quenched by oxygen, but the vinyl cation reacts rapidly with nucelophiles such as alcohols. These properties exclude T_{410} from being a vinyl cation. Moreover, for 1-(p-methyl-phenyl)-2-dimethylvinyl bromide, a flexible styrene analogue of Br_2-stilbene, the lifetime of the vinyl cation in acetonitrile was estimated to be as short as 8 ns [23].

(6) Assignment of T_{410} to $^3DPA^*$ is supported by the following. First, the absorption spectra of $^3DPA^*$ and T_{410} are almost identical (Fig. 3). Secondly, T_{410} is quenched by triplet quenchers such as ferrocene, 1,3-pentadiene and oxygen at rates similar to those for $^3DPA^*$ (Table 2). Thirdly, the decay is essentially first order; differences in the observed lifetimes of $^3DPA^*$ and T_{410} are probably due to quenching of the transient by DPA and X_2-stilbene (or the radicals initiated by atomic X) respectively. For $^3DPA^*$ self-quenching was observed (see above) and the transient lifetimes represent only lower limits, as shown by the comparison upon conventional flash photolysis.

4.2. Mechanism of photodehalogenation

The increase in Φ_{DPA} in the order Cl_2-, Br_2- and I_2-stilbene is in agreement with the strength of the C—X bond [30]. Formation of DPA occurs via the excited trans singlet state of Br_2- or I_2-stilbene, bypassing the $^3S_t^*$ state (Scheme 1). A triplet route is excluded, since DPA was not observed under sensitized excitation of X_2-stilbene. The $^3DPA^*$ state may be formed from Br_2- or I_2-stilbene by absorption of one photon or two photons. The former possibility is excluded, since otherwise a linear dependence of the initial part of ΔA_{410} vs. I_L should be observed. This linear dependence was found for DPA but not for X_2-stilbene (Fig. 4). Simultaneous absorption of two photons is likewise excluded, since DPA in the ground state was also produced from X_2-stilbene on steady state irradiation and Φ_{DPA} was found to be independent of the light intensity (254 nm). It is therefore concluded that $^3DPA^*$ is formed via consecutive absorption of two photons.

The proposed mechanism is illustrated in Scheme 1. DPA is formed from Br_2- or I_2-stilbene after absorption of one photon and immediate splitting of the two C—X bonds. Elimination of X_2 or $X^{\cdot}$, followed by formation of X_2, probably

occurs from a twisted conformation of the first excited singlet of X_2-stilbene. This process is suggested to be quite fast, since $^3DPA^*$ and necessarily the DPA ground state are formed within 20 ns. A likely possibility is a cage effect, which would explain the temperature dependence of Φ_{DPA}, being larger at elevated temperatures and smaller at lower temperatures (see Section 3.1). A cage reaction for heterolytic release of atomic Br or I is well known for 5-X-pyrimidines such as 5-bromouracil, 5-iodouracil and derivatives [31].

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