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Journal of Photochemistry and Photobiology A: Chemistry 138 (2001) 275–280

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

4,4′-Diaminostilbene-2,2′-disulfonate (DSD) behaviour: under irradiation in water. Decrease of its activity as a fluorescent whitening agent

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Received 28 July 2000; received in revised form 13 October 2000; accepted 23 October 2000

Abstract

The behaviour of 4,4′-diaminostilbene-2,2′-disulfonate (DSD), a fluorescent whitening agent, in aqueous solution was investigated under monochromatic irradiation ($\lambda_{\mathrm{irr.}} = 313$, 334 and 365 nm) at room temperature; depending on the pH, two different behaviours were observed. At pH ≥ 4.2, with the predominant molecular form (DSD), only the photoisomerisation process occurs leading to a photostationary state rich in *cis*-isomer, a non-emitting compound. At pH ≤ 3.0, with the diprotonated form ($DSDH_2^{2+}$), the photoisomerisation process was followed by a slow photodegradation of the resulting *cis*-isomer. For prolonged irradiation, the total disappearance of $DSDH_2^{2+}$ was observed. The nature of the photoproducts depended on the irradiation wavelength. The initial quantum yields (ϕ) of the direct *trans*–*cis* photoisomerisation were measured and the absorption spectra of the *cis*-isomers were calculated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 4,4′-Diaminostilbene-2,2′-disulfonate; FWA (fluorescent whitening agent); pH; Photoisomerisation; Photodegradation

1. Introduction

4,4′-Diaminostilbene-2,2′-disulfonate (DSD) is widely used as a fluorescent whitening agent (FWA) in textile, paper and plastic manufacturing and in household detergents, because of its property to transform part of the UV–visible solar irradiation in a blue fluorescence light, giving the feeling of bright whiteness.

The contamination of aquatic bodies by potential harmful organic chemicals such as FWAs is one of the great environmental problems: tons per year of these compounds are discharged into sewage treatment plants or directly into the aquatic environment world-wide. The FWAs are not easily degradable by the wastewater treatment and Poiger et al. [1], Stoll and Giger [2] have identified in rivers and in bank filtrates some aromatic sulfonates derivatives coming from their degradation after drinking water treatment. The major sink in the environment for such absorbing compounds is possibly a direct photodegradation by sunlight in surface waters. In fact, Hoigné and co-workers [3] measured the degradation quantum yields and the half-life of two diaminostilbenes, they were about 10^{-4} and shorter than 5 h in sunlit natural waters, respectively. Our aim was first to investigate the photochemical behaviour of DSD under environmental conditions in relation to its role of FWA, and then the degradation photoinduced by iron(III).

The mechanism of photoisomerisation of stilbene has been extensively studied in the last few decades, both experimentally and theoretically [4–8]; it is now well understood and occurs by rotation about the stilbene central double bond. In fact, it is generally accepted that the light-induced reversible isomerisation of *trans*-stilbene proceeds either from the lowest excited singlet state $^1t^*$ or through the twisted singlet intermediate $^1p^*$ (“phantom” state).

In this paper, we report the photochemical behaviour of DSD not reported so far upon irradiation by wavelengths present in the solar emission; when dealing with FWA like DSD, it is of major interest to know the percentage of *trans*-isomer in the photostationary state, this being the only fluorescent isomer.

2. Reagents and solvents

4,4′-Diaminostilbene-2,2′-disulfonate (*trans*-DSD) was an Acros product (95%). The purity of the product was controlled by ^1H NMR in $(CD_3)_2SO$: $\delta = 1.10$ ppm, 4 protons: H from the two NH_2 groups; aromatic ring: $\delta = 7.25$ ppm, dd, 2 protons, H5 and H5′; $\delta = 7.68$ ppm, d, 2 protons, H6 and H6′; $\delta = 7.74$ ppm, d, 2 protons, H3 and H3′ and

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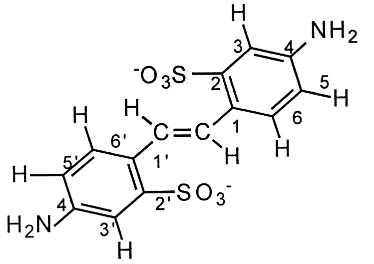
PII: S1010-6030(00)00400-7

Table 1
Photonic fluxes as a function of wavelength

$\lambda_{irr.}$ (nm)	365	334	313
I_0 (10^{15} photons/s/cm^2)	4.1	1.3	1.9

$\delta = 8.1$ ppm, s, 2 protons, H_{trans} from the double bond.



Perchloric acid was a Merck product (70%), NaOH was a Prolabo product (97%), and hydrochloric acid (min. 32%) and methyl sulfoxide-d6 (99.9% D) were Acros products.

All the solutions were prepared with ultrapure aerated water (Millipore αQ, resistivity = 18.2 MΩ). The pH was adjusted with NaOH, H_3PO_4 or HCl and controlled with an ORION pHmeter to 0.01 pH unit. The ionic strength was not controlled.

DSD concentrations ranged between 4.75×10^{-6} and 4×10^{-5} M, the maximum of solubility being 4×10^{-5} M due to the low polarity of the molecule.

3. Apparatus

A high-pressure mercury lamp (OSRAM HBO 200 W) with a grating monochromator (Bausch and Lomb) was used for irradiations at 313, 334, and 365 nm. The beam was parallel and the reactor was a cylindrical quartz cell of 1, 2 or 5 cm path length. The photonic fluxes were measured by ferrioxalate actinometry [9] (Table 1).

UV–visible spectra were recorded on a Cary 3 double-beam spectrophotometer and emission spectra on a Perkin-Elmer fluorimeter.

High performance liquid chromatography (HPLC) experiments were carried out using a Waters chromatograph equipped with a photodiode array detector (Waters 990) giving the UV–visible spectrum at any time (sampling time = 80 ms). The flow rate was 1 ml min^{-1} and the column was a Waters Spherisorb (5 μm) of 25 cm length. The eluent was water with either 3 or 1‰ H_3PO_4, or $NaClO_4$ (1×10^{-2} M). The acidification (pH = 1.7 or 2.3) of the eluent or the presence of Na^+ cations permitted a good separation of the two isomers.

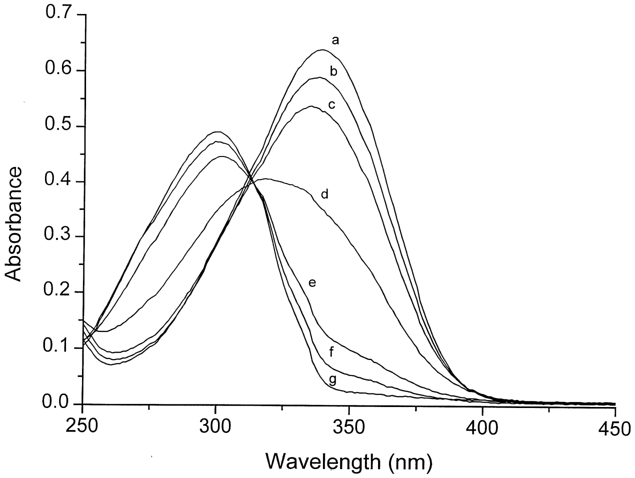


Fig. 1. Absorption spectra of DSD in water at room temperature (concentration 2×10^{-5} M). The pH values of solution are as follows: curve a, 4.8; curve b, 4.7; curve c, 4.1; curve d, 3.5; curve e, 2.8; curve f, 2.5 and curve g, 1.6.

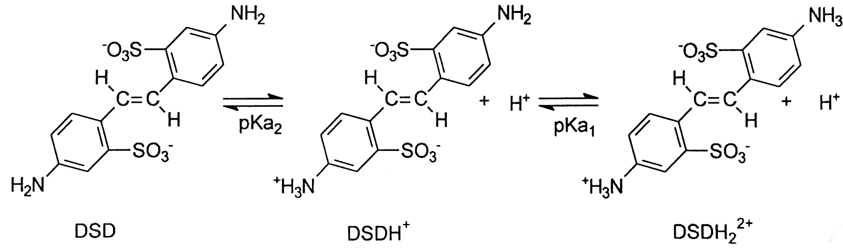
^{1}H NMR spectra were recorded with a Brucker AC 400 spectrometer and mass spectra with a Hewlett-Packard 5989.

4. Results

4.1. Characterisation of 4,4′-diaminostilbene-2,2′-disulfonate (DSD, trans form) in solution

Due to the relatively poor solubility of DSD isomer, the aqueous solution (concentration 4×10^{-5} M) was obtained by stirring at room temperature for 15 h; the so obtained solution is thermally stable (for a few days at room temperature in the dark). The acidity of the solution (pH around 4.5 for a concentration equal to 2×10^{-5} M) was fixed by the sulfonate groups of the molecule.

The presence of two isobestic points in the absorption spectra (in Fig. 1 between curves a–c and between curves d–g) means that DSD exists in three different forms according to the pH: DSD, its monoprotonated ($DSDH^+$) and diprotonated ($DSDH_2^{2+}$) forms. This two-step proton dissociation constant has been already reported by Zhao et al. [10] for 4,4′-diaminostilbene (DAS).



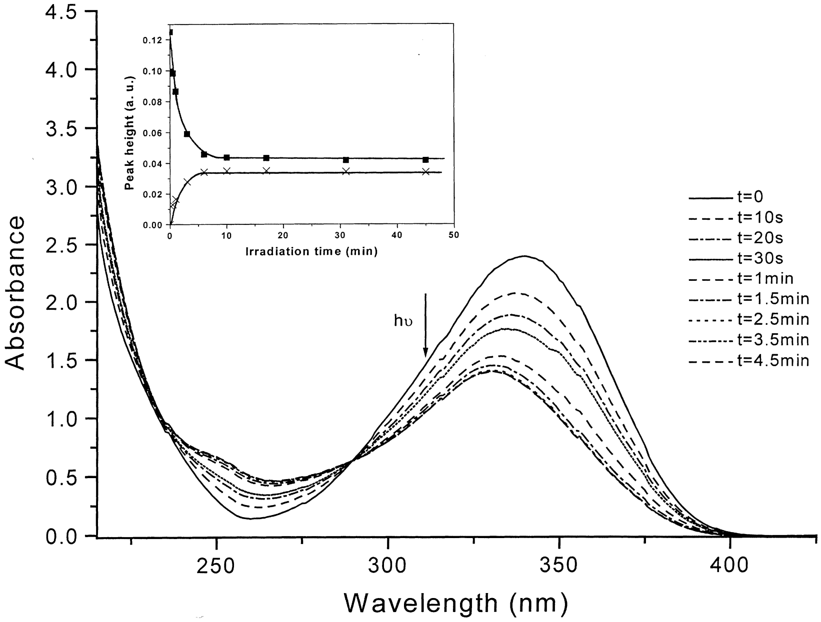


Fig. 2. Spectral evolution of DSD solution, 4×10^{-5} M, pH = 6.0, $\lambda_{irr.} = 313$ nm; insert: kinetics of (×) *cis*-appearance and (■) *trans*-DSD disappearance (detected at 300 nm).

pK_a values of 4.5 and 3.7 have been calculated for the first protonation and second protonation correspondingly, by monitoring the absorbances at 265, 300 and 337 nm as a function of pH.

The diprotonated form $DSDH_2^{2+}$ is predominant at pH < 3.0 whereas the molecular form DSD is mainly present at pH > 4.2. At any pH value between pK_{a1} and pK_{a2}, the solution contains the three species; so it was difficult to define the spectra of the DSD monocation and to study its photochemical behaviour. On the other hand, the molecular and diprotonated forms are well-defined and their photochemical behaviour appear to be significantly different.

In all cases, the UV–visible spectrum of the DSD presents an absorption up to 420 nm (Figs. 2 and 6) which made possible its role as FWA upon solar light irradiation.

5. Photochemical behaviour of 4,4′-diaminostilbene-2,2′-disulfonate

5.1. The molecular form at pH = 6.0

The UV spectrum of *trans*-DSD (Fig. 2) presents an absorption band at $\lambda_{max} = 338$ nm ($\varepsilon_{max} \approx 30\,400\ M^{-1}\ cm^{-1}$). Upon irradiation, at pH = 6.0 (molecular-form predominant) the *trans–cis* isomerisation was observed and a photostationary state was reached. This process was very fast and took place within only a few minutes in our experimental conditions. We confirmed the isomerisation process by using HPLC. We followed the decrease of the *trans*-form (retention time = 5.2 min) and the only appearance of the *cis*-form (retention time = 2.1 min), confirmed by the UV–visible spectrum (cf. later).

The mixture was photostable for long irradiation times (Fig. 2). A similar result was obtained for irradiation at 334 and 365 nm.

The absorption spectrum of the *cis*-form was calculated by using Fischer's method [11], which is valid for phototransformation with a photostationary state stable both thermally and photochemically. According to Fisher's method, provided the ratio $\Phi_{t \to c}/\Phi_{c \to t}$ does not differ at two different wavelengths, the absorption spectrum of molecular *cis*-DSD can be calculated (Fig. 3).

The calculated *cis*-form presents an absorption band at $\lambda_{max} = 322$ nm ($\varepsilon_{max} \approx 12\,700\ M^{-1}\ cm^{-1}$) and a shoulder at 247 nm; the maximum in the near UV domain is strongly blue shifted when compared to the *trans* absorption.

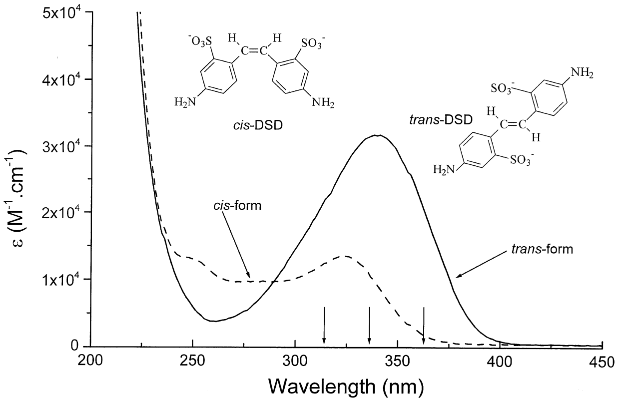


Fig. 3. Absorption spectra of solutions in water at room temperature, pH = 6.0, (—) spectrum of *trans*-DSD, (- - -) calculated spectrum of *cis*-DSD. Arrows indicate the wavelengths of monochromatic irradiation.

Table 2
Quantum yield of *trans*⇌*cis* isomerisation, $\lambda_{\mathrm{irr.}} = 313\,\mathrm{nm}$, pH = 6.0

[DSD] × 10^{-5} M	Equilibrium % *cis*	$\Phi^0_{\mathrm{t}\rightarrow\mathrm{c}}$	$\Phi^0_{\mathrm{c}\rightarrow\mathrm{t}}$
0.8	65	0.42	0.39
1.9	66	0.45	0.40
3.8	66	0.44	0.41

Table 3
Quantum yield of *trans*⇌*cis* isomerisation, $\lambda_{\mathrm{irr.}} = 334\,\mathrm{nm}$, pH = 6.0

[DSD] × 10^{-5} M	Equilibrium % *cis*	$\Phi^0_{\mathrm{t}\rightarrow\mathrm{c}}$	$\Phi^0_{\mathrm{c}\rightarrow\mathrm{t}}$
1.9	73	0.47	0.46

Table 4
Quantum yield of *trans*⇌*cis* isomerisation, $\lambda_{\mathrm{irr.}} = 365\,\mathrm{nm}$, pH = 6.0

[DSD] × 10^{-5} M	Equilibrium % *cis*	$\Phi^0_{\mathrm{t}\rightarrow\mathrm{c}}$	$\Phi^0_{\mathrm{c}\rightarrow\mathrm{t}}$
0.8	93	0.42	0.41
1.9	93	0.40	0.37
3.8	94	0.43	0.37

The quantum yields were calculated for three different irradiation wavelengths (313, 334 and 365 nm) by using the results obtained with Fischer's method. At three different concentrations in DSD, the initial quantum yield was equal to 0.44 for the *trans* → *cis* isomerisation and equal to 0.40 for the reverse; there was a good agreement between the Φ values and percentage obtained under these different conditions (Tables 2–4).

A photostationary state with more than 65% *cis*-isomer was obtained under irradiation at 313 nm and more than 90% under irradiation at 365 nm. It is of interest to note that the relative percentage of *cis*- and *trans*-isomers at the photostationary state control the fluorescence. As already mentioned, only the *trans*-DSD is an emitting species upon excitation. This was confirmed by the evolution of the emission spectrum of a solution of DSD. Fig. 4 shows the decrease of the emission upon irradiation. This rapid extinction (about 95% in 1 min at 365 nm) is connected to the isomerisation of *trans*-DSD into non-emitted *cis*-form. As a result, upon solar irradiation, DSD would lose an important part of its emitting properties and so become a far less efficient FWA.

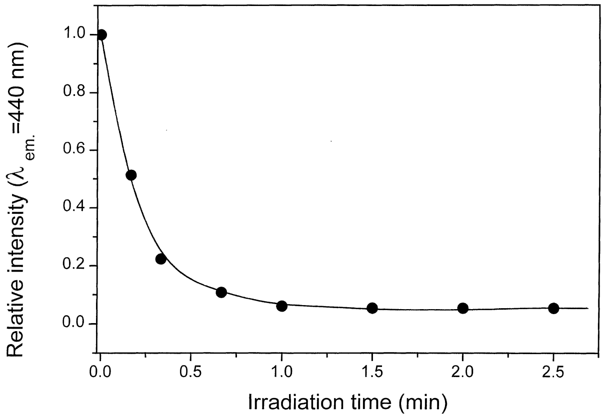


Fig. 4. Relative intensity of emission of DSD ($\lambda_{\mathrm{em.}} = 445\,\mathrm{nm}$) as a function of irradiation time, concentration 4×10^{-5} M, pH = 6.0, $\lambda_{\mathrm{irr.}} = 365\,\mathrm{nm}$, $\lambda_{\mathrm{exc.}} = 360\,\mathrm{nm}$.

5.2. *The diprotonated form* pH = 1.7

The UV spectrum of *trans*-$\mathrm{DSDH_2}^{2+}$ presents two absorption bands at $\lambda_{\max} = 299\,\mathrm{nm}$ ($\varepsilon_{\max} \approx 24\,000\,\mathrm{M^{-1}\,cm^{-1}}$) and at $\lambda_{\max} = 206\,\mathrm{nm}$ ($\varepsilon_{\max} \approx 30\,900\,\mathrm{M^{-1}\,cm^{-1}}$) and a shoulder at 230 nm (Fig. 6).

In contrast to the behaviour observed at pH = 6.0, the irradiation of *trans*-$\mathrm{DSDH_2}^{2+}$ at pH = 1.7 results in complicated kinetics, caused by the superposition of the photochemical *trans* to *cis* isomerisation and the subsequent photodecomposition of the diprotonated *cis*-isomer.

Fig. 5 represents the evolutions of *cis*- (retention time = 2.6 min) and *trans*-forms (retention time = 5.4 min) as a function of the irradiation time. In this case, the fast photoisomerisation process occurred too but followed by a slow disappearance of the *cis*-isomer; the concentration of *trans*-$\mathrm{DSDH_2}^{2+}$ decreased fastly and the concentration of *cis*-$\mathrm{DSDH_2}^{2+}$ ran through a maximum value and decreased thereafter with irradiation time. In less than 3 h, FWA was completely photodegraded. A similar result was obtained for irradiation at 334 and 365 nm, but for longer irradiation.

As it was previously mentioned, upon irradiation (at 313, 334 and 365 nm) of the protonated form, there is first a *trans* ⇌ *cis* isomerisation until a pseudophotostationary state and then a concomitant photodecomposition of the *cis*-isomer. The precise determination of the *cis*'s UV–visible spectrum by the Fischer's method was impossible because of the presence of a subsequent reaction;

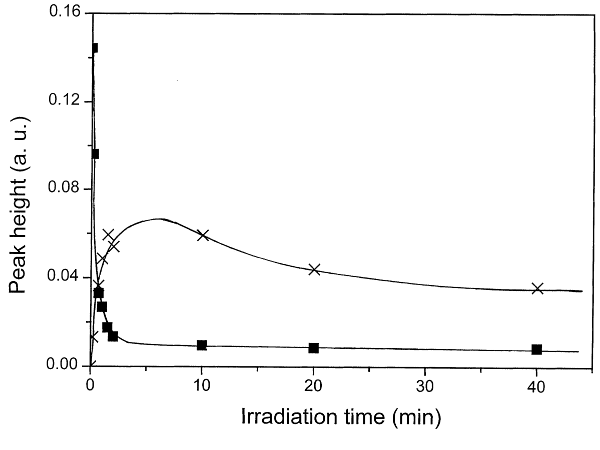


Fig. 5. Kinetics of (×) *cis*- appearance and (■) *trans*-$\mathrm{DSDH_2}^{2+}$ disappearance, pH = 1.7, concentration 4×10^{-5} M, irradiation at 313 nm (detected at 300 nm).

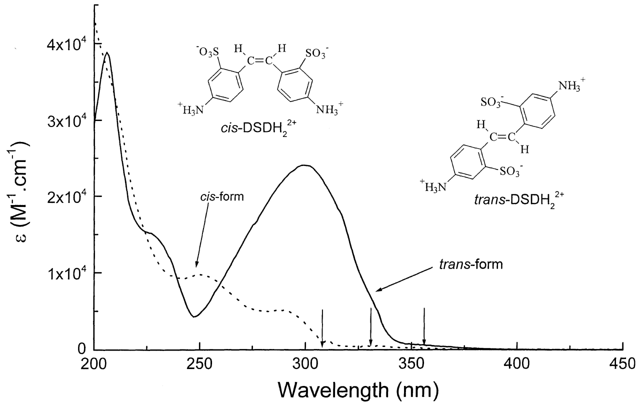


Fig. 6. Absorption spectra of solutions in water at room temperature, pH = 1.7, (—) spectrum of *trans*-$DSDH_2^{2+}$, (- - -) calculated spectrum of *cis*-$DSDH_2^{2+}$. Arrows indicate the wavelengths of monochromatic irradiation.

the photodegradation of the *cis*-isomeric form. The formation of two major photoproducts observed by HPLC showed clearly that the conditions required for the application of Fischer's method were not fulfilled. The method used in this case, consisted in subtracting the spectrum of *trans*-$DSDH_2^{2+}$ from that of a mixture containing known amounts of *trans*- and *cis*-$DSDH_2^{2+}$ obtained by short irradiation of a solution of pure *trans*-$DSDH_2^{2+}$, assuming the photodegradation to be negligible in the early stages of the reaction. The concentrations were determined by HPLC.

The *cis*-$DSDH_2^{2+}$ spectrum (Fig. 6) presents two bands at λ_{max} = 251 nm ($\varepsilon_{max} \approx 9700\,M^{-1}\,cm^{-1}$) and at λ_{max} = 290 nm ($\varepsilon_{max} \approx 5100\,M^{-1}\,cm^{-1}$): a large blue shift was observed again.

The quantum yields of the *trans* → *cis* photoisomerisation $\Phi^0_{t\to c}$ were estimated to be 0.48 under irradiation at 365 nm and 0.32 at 334 nm (Table 5) and the pseudophotostationary state is made of almost pure *cis*-isomer that then undergoes a degradation. Accordingly it is impossible to make a precise calculation of $\Phi^0_{c\to t}$ nevertheless it was very low.

The evolution of the absorbance at 251 nm represented on Fig. 7 shows a rapid growth followed by a much slower increase. According to the observations in HPLC analysis, the rapid growth of the absorbance can be attributed to the fast photoisomerisation *trans* to *cis*-isomer, 251 nm being λ_{max} of *cis*-$DSDH_2^{2+}$. The second part of the curve can be attributed to the involvement of an additional photochemical reaction likely DSD degradation observed from the *cis*-form (cf. HPLC results), making the whole mechanism very complicated.

Table 5
Quantum yields of *trans*⇌*cis* isomerisation of DSD vs. the wavelength, 3.8×10^{-5} M, pH = 1.7

$\lambda_{irr.}$ (nm)	Equilibrium % *cis*	$\Phi^0_{t\to c}$	$\Phi^0_{c\to t}$
334	99	0.32	0.02
365	99.5	0.48	≃ 0.002

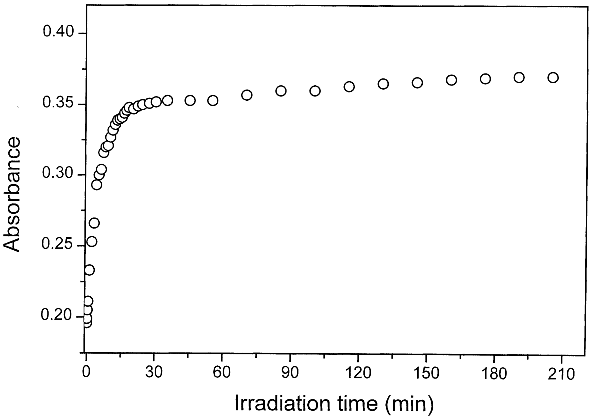


Fig. 7. Evolution of absorbance at 251 nm as a function of irradiation time, *trans*-$DSDH_2^{2+}$, concentration 4×10^{-5} M, $\lambda_{irr.}$ = 334 nm, pH = 1.7.

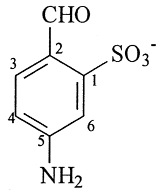
5.3. *Identification of the degradation products (*$DSDH_2^{2+}$ *at* pH = 1.7*)*

Upon irradiation at 365 nm, two decomposition products appeared, identified from ^1H NMR and mass spectra. Both photoproducts appeared as primary products.

- Photoproduct 1.

  MS: main peak, $m/e = 200$.
  ^{1}**H** NMR (D_2O). δ: 3.60 (2H, multiplet, $-NH_2$), δ: 7.05 (1H, redoubled doublet, J_1 = 8 Hz, J_2 = 1.6 Hz, H_4), δ: 7.24 (1H, doublet, J_1 = 6.5 Hz, H_3), δ: 7.78 (1H, singlet, H_6), δ: 9.84 (1H, singlet, CHO).

  The spectra features are in agreement with the aldehydic derivative.



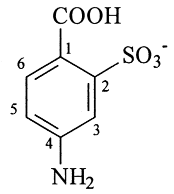
5-amino-2-formyl-benzenesulfonic acid

  A pK_a value of 3.6 for this product has been determined by monitoring the absorbance at 254 nm in a function of pH.

- Photoproduct 2.

  MS: main peak, $m/e = 216$.
  ^{1}**H** NMR (D_2O). δ: 3.80 (2H, multiplet, $-NH_2$), δ: 7.35 (1H, redoubled doublet, J_1 = 8.8 Hz, J_2 = 2.4 Hz, H5), δ: 7.65 (1H, doublet, J_1 = 2.3 Hz, H6), δ: 8.25 (1H, doublet, J_1 = 8.5 Hz, H3), δ: 10.70 (1H, singlet, COOH).

  The features are in agreement with the corresponding carboxylic derivative.



4-amino-2-sulfo-benzoic acid

Two pK_a values of 3.5 and 1.1 for this product have been determined by monitoring the absorbance at 328 nm in a function of pH.

Those products result from the oxidative cleavage of the double bond. A similar process has been already reported for the *trans*-4,4′-diacetamidostilbene (DAS) [12]; this derivative in solution undergoes a rapid photoisomerisation, followed by a degradation which gives rise to 4-acetamidobenzaldehyde and 4-acetoamidobenzoic acid. Hoigné and co-workers [3] who investigated the direct photolysis of FWAs (DAS-type), at pH = 8.0 in solution observed together with the formation of the aldehydic derivative, the formation of alcohol instead of the carboxylic derivative.

Upon irradiation at 313 and at 334 nm, the chromatogram of an irradiated acidic solution was far more complicated with several peaks, among them, photoproduct 2 (carboxylic derivative) formed in low yield.

6. Conclusion

The *trans* $\rightleftharpoons$ *cis* isomerisation of DSD in aqueous solution strongly depends on the pH. In mildly acidic or neutral solution ($pH \geq 4.2$), the main species (molecular DSD) only undergoes a *trans–cis* isomerisation process with high and similar quantum yields. In acidic solution ($pH \leq 3.0$), the quantum yield of *trans* → *cis* isomerisation is still high but, under these conditions, the *cis*-isomer ($DSDH_2^{2+}$) undergoes a subsequent degradation. In both cases, due to the blue shifted absorption of the *cis*-isomer the photostationary state (or pseudo) is rich in the *cis*-isomer the non-emitting species. In neutral solutions, the percentage of *cis*-isomer goes from 65% at 313 nm up to 95% at 365 nm. This phenomenon implies that upon irradiation by solar light and in environmental conditions of pH, only a few percents of the starting concentration in DSD plays the role of FWA, e.g. a waste of material and an unnecessary contamination of the aquatic compartment.

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