ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 151 (2002) 137–143

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Photochemical study of 4,4′-dinitrostilbene-2,2′-disulfonate (DSD) degradation in water

Anita Rachel, Bernadette Lavédrine, Jean-Pierre Aguer, Pierre Boule*

Laboratoire de Photochimie Moléculaire et Macromoléculaire, Université Blaise Pascal, Ensemble Universitaire des Cézeaux,
UMR 6505, F-63177 Aubière Cedex, France

Received 20 March 2002; accepted 26 March 2002

Abstract

When 4,4′-dinitrostilbene-2,2′-disulfonate (DSD) is submitted to UV or visible light in aqueous solution, the main photochemical process is a reversible *trans–cis* isomerisation, the *cis* form absorbs at shorter wavelength than the *trans* isomer. The UV spectrum of *cis* form may be obtained not only by Fischer's method but also by using HPLC with UV detection at isosbestic point (311 nm). Quantum yields were evaluated at 0.30 and 0.24 for *trans* → *cis* and *cis* → *trans* isomerisation, respectively.

Photolysis also occurs but only with a very low quantum yield [$(2.2 - 2.4) \times 10^{-4}$]. For this reason photocatalysis may be useful to accelerate the elimination of DSD from waste waters. Photocatalytic transformation is more efficient with TiO_2 Degussa P25 than with TiO_2 Millennium PC50 in spite of pure anatase composition of the latter. Immobilization of TiO_2 on pumice stone is an interesting method to eliminate the problem of filtration implied by the use of slurries. To evaluate disappearance by UV detection it is recommended to detect at isosbestic point to do not interfere with isomerisation.

Keywords: 4,4′-Dinitrostilbene-2,2′-disulfonate; Photocatalytic transformation; *Trans–cis* isomerisation photolysis

1. Introduction

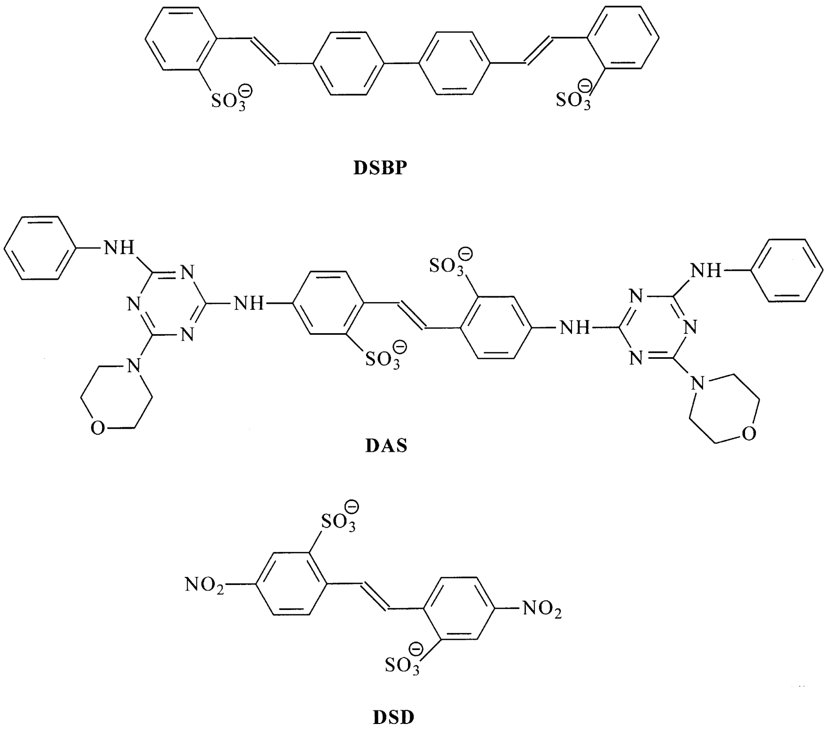
Stilbene derivatives correspond to a large group of compounds. Most of them are widely used as fluorescent whitening agents (FWA) in textiles, detergents, paper or plastics to make products whiter and brighter by compensating for the yellowish shade of materials. Two FWAs (Fig. 1) strongly dominate worldwide production of FWAs, they were respectively produced at 3000 and 14,000 t per year in 1992 [1]. Fluorescent and brightening properties do not represent the only interest towards these compounds. For example stilbene derivatives like 4,4′-dinitrostibene-2,2′-disulfonate (DSD) (Fig. 1) are used as intermediate in the synthesis of dye [2]. As a consequence of this extensive utilization, stilbenes constitute an important source of pollution in natural waters and soil. In contrast to their biological resistance, photochemical degradation may represent an efficient process for their elimination [3]. Many works deal with the subject and FWAs were extensively studied. Photochemical degradation is preceded by a fast reversible *trans–cis* isomerisation reaction. Ever since the study conducted by Saltiel [4–6], this process is well known. Three mechanisms are possible to explain the *trans* → *cis* isomerisation. The commonly accepted mechanism involves a rotation around the ethylenic bond in the first excited singlet state to a twisted geometry in which the crossing with the ground state is forbidden. Alternatively, the *trans* → *cis* isomerisation may be explained by the formation of the lowest singlet intermediate $^1p^*$ (phantom). The nature of the substituent as well as the solvent have a strong influence on the mechanisms [7–9]. The rate of *trans* → *cis* isomerisation reaction is increased by both polar solvents and polar substituents in the case of weak donor–acceptor substituents. The presence of a strong donor substituent in the 4 position of the aromatic ring leads to a destabilization of the transition between the singlet excited state and the twisted intermediate and thus, there is a negative effect on the isomerization reaction. In water, photoisomerisation of some stilbenedisulfonate derivatives has been studied. The quantum yields of *trans* → *cis* isomerisation were determined either by HPLC or by changes in the UV spectrum absorption and they lie in the range 0.30 to 0.45 depending on the substituent [10–12].

Further degradation is much slower, Hoigné and co-workers [13] measured the degradation quantum yields

---

* Corresponding author. Tel.: +33-473407176; fax: +33-473407700.
E-mail address: pierre.boule@univ-bpclermont.fr (P. Boule).

1010-6030/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S1010-6030(02)00144-2



DSBP

DAS

DSD

Fig. 1. Structure of DSBP and DAS, two nitrostilbene derivatives used as fluorescent whitening agents and DSD used as intermediate in the synthesis of dye.

and the half-life of two diaminostilbenes, they obtained 10^{-4} for the quantum yield and the half-life in natural water exposed to sunlight was evaluated at 5 h.

The aim of this work is to study direct and photocatalytic degradation of 4,4′-dinitrostibene-2,2′-disulfonate as well as its photoisomerisation. Methods combining spectrophotometry and HPLC are proposed for the determination of the UV spectrum of *cis* form and for the determination of quantum yields. Two different TiO_2 are compared for the photocatalytic transformation.

2. Experimental parts

2.1. Chemicals and supports

4,4′-Dinitrostilbene-2,2′-disulfonate disodium salt (*trans*-DSD) was a TCI product (95%). Tetrabutylammonium hydrogen sulfate (TBA) Fluka (>97%) was used for HPLC analyses. All the solutions were prepared with ultra pure air-saturated water (Milli-Q, resistivity $\geq 18.2\,M\Omega$).

The photocatalytic transformation of DSD was studied with two different TiO_2: Degussa P25 (anatase/rutile 70/30; surface area $55\,m^2\,g^{-1}$) and Millennium PC50 (anatase surface area $45 \pm 5\,m^2\,g^{-1}$). They were used as slurries or immobilized on pumice stone (slice $16\,cm^2$; $e = 6\,mm$), Volvic lava (slice $14\,cm^2$; $e = 10\,mm$), red brick or white cement disk ($\phi = 52\,mm$; $e = 10\,mm$).

Table 1
Photonic fluxes as a function of wavelength

λ_{irr} (nm)	313	365
I_o (10^{15} photons $s^{-1}\,cm^{-2}$)	1.34	2.30

2.2. Irradiation

Direct photolysis was carried out with a high pressure mercury lamp (OSRAM HBO 200 W) equipped with a Bausch and Lomb monochromator. The beam was parallel and the reactor was a cylindrical quartz cell of 1 cm path length. The photonic fluxes were measured by ferrioxalate actinometry (Table 1).

For photocatalytic transformation, solutions of $2.0 \times 10^{-5}\,mol\,l^{-1}$ were magnetically stirred in the presence of TiO_2 ($2\,g\,l^{-1}$) and exposed to UV light in the range 290–436 nm using fluorescent lamps TLD 15W/05 in crystallizer ($\phi = 53\,mm$) covered with a watch glass in Pyrex. The photon flow received was evaluated at 3.4×10^{15} photons $cm^{-2}\,s^{-1}$ using potassium ferrioxalate as the actinometer.

2.3. Immobilization of TiO_2

Several techniques were used for immobilization of TiO_2 on solid support:

(1) Sol–gel dip-coating using titanium diisopropoxide bis-acetylacetonate, isopropanol and water as described

elsewhere [14]. Six layers were deposited in order to obtain a film in the range 0.1–1.0 μm on a disk of red brick or white cement. It was calcined at 450 °C during 5 h in order to obtain anatase form of TiO_2.

(2) Impregnation of TiO_2 on pumice stone or Volvic lava.

A suspension of TiO_2 P25 (5% in water) sonicated for a better dispersion, was spread on the support with a brush and maintained under reduced pressure (≈0.1 bar) during 1 min to eliminate air from pores. After drying the support was washed to eliminate the excess of TiO_2 and dried again.

2.4. Analyses

Spectra of solutions were recorded on a CARY 3 VARIAN spectrophotometer. All the samples were filtered by a Millipore filter (0.45 μm) prior to analysis in order to remove TiO_2 from the slurry. Analyses of samples were carried out by HPLC–Waters 996 equipped with a photodiode array detector that gives a UV–VIS spectrum of the different compounds present in the solution. Column was Microsorb RP-18, 5 μm and the eluent a mixture of methanol/water (55/45) v/v with a flow rate 1 ml min^{-1}. Tetrabutylammonium hydrogen sulfate (TBA) 10^{-2} mol l^{-1} was added to water in order to obtain a good separation of peaks.

3. Photoisomerisation

3.1. Spectrum of *cis* form

The absorption spectrum of the *cis* form can be calculated from Fischer's method [15]. This method is based on the comparison of the stationary photochemical equilibria reached by irradiation at two different wavelengths. The stationary concentrations correspond to the equality between *trans* → *cis* and *cis* → *trans* isomerisation rates:

$$\phi_{\mathrm{t}\to\mathrm{c}}[trans]\varepsilon_{\mathrm{t}} = \phi_{\mathrm{c}\to\mathrm{t}}[cis]\varepsilon_{\mathrm{c}} \qquad (1)$$

where [*trans*] and [*cis*] are the concentrations of both forms, ε_{t} and ε_{c} the molar absorption coefficients and $\phi_{\mathrm{t}\to\mathrm{c}}$ and $\phi_{\mathrm{c}\to\mathrm{t}}$ both quantum yields of photoisomerisation. When solutions are irradiated at isosbestic point, $\varepsilon_{\mathrm{t}} = \varepsilon_{\mathrm{c}}$ thus:

$$\frac{\phi_{\mathrm{t}\to\mathrm{c}}}{\phi_{\mathrm{c}\to\mathrm{t}}} = \frac{[cis]}{[trans]}$$

In the present study, solutions were irradiated on mercury lines at 313 and 365 nm (Fig. 2). An isosbetic point appears at 311 nm. With Fischer's method it is possible to calculate the percentage of *cis* form by irradiating at 313 nm and at 365 nm. The percentage of *cis* form in the irradiated solutions (48.4 at 313 nm and 84.7 at 365 nm) was deduced as well as the spectrum of *cis* form (Fig. 3). Both irradiation wavelengths led to very similar spectra. An alternative method involving HPLC was also used : it was observed that both isomers can be separated by HPLC using C_{18} column and a mixture 55% MeOH/45% water + 10^{-2} mol l^{-1} TBA (Fig. 4). Retention times were, respectively 10 and 12 min for *trans* and *cis* form. When UV detection of HPLC is set exactly at isosbestic point (311 nm) both forms are detected with the same sensitivity and peak areas are proportional to concentrations. It was deduced that the percentage of *cis* form at the photostationary equilibrium are 55 and 87 when solutions are irradiated at 313 and 365 nm, respectively. These values are less subject to error than those

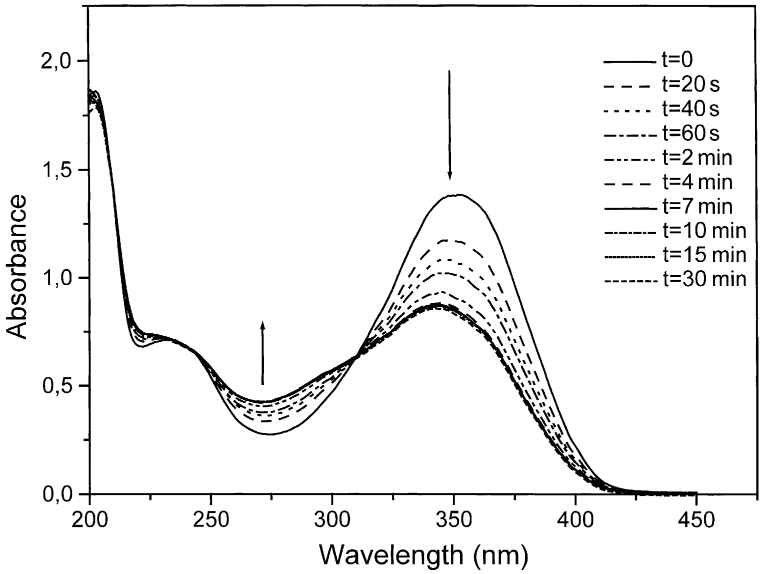


Fig. 2. Evolution of the UV spectrum of a solution of DSD 2×10^{-5} mol l^{-1} irradiated at 313 nm.

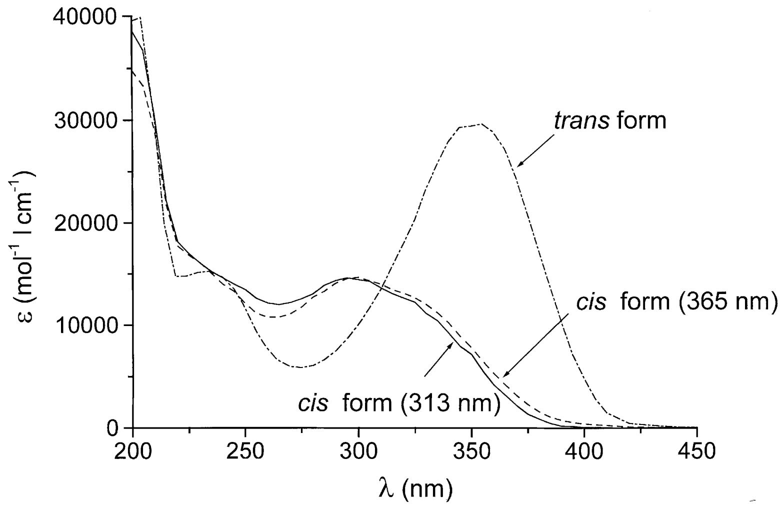


Fig. 3. UV spectrum of *cis* form of DSD deduced from photostationary state at 313 and 365 nm by Fischer's method.

obtained with Fischer's method since they are directly deduced from experimental data, whereas the latter result from a complex calculation. This method lead to similar spectrum for *cis* form when compared to the Fischer method. It is in accordance with the spectrum obtained with HPLC photodiode array detector.

3.2. Quantum yield

The quantum yield $\phi_{t\to c}$ was calculated from the kinetics of phototransformation at 365 nm. The transformation rate was deduced from the evolution of UV absorbance at 350 nm with irradiation time. It is much more reproducible than HPLC measurements for low conversion extent. The initial transformation rate is obtained by dividing the initial slope of the graph : Abs (absorbance) 350 nm versus time, by $(\varepsilon_{t350\,nm} - \varepsilon_{c350\,nm})$.

Then

$$\phi_{t\to c} = \frac{\text{slope}}{(\varepsilon_{t350\,\mathrm{nm}}-\varepsilon_{c350\,\mathrm{nm}}) \times I_{0365\,\mathrm{nm}} \times (1-10^{\mathrm{Abs}\,365\,\mathrm{nm}})} \tag{2}$$

The value of $\phi_{c\to t}$ is deduced from relation (1) at 313 nm for a better accuracy since 313 nm is very near isosbestic point and the ratio $\varepsilon_t/\varepsilon_c$ is near unity. It was deduced that $\phi_{t\to c} = 0.30$ and $\phi_{c\to t} = 0.24$ that is in good agreement with values given in literature for isomerisation of other stilbene derivatives [10,12].

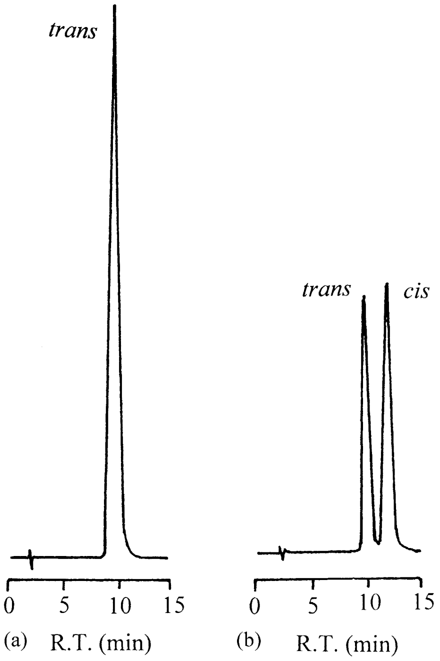


Fig. 4. HPLC separation of DSD *trans* and *cis* isomers detection at 311 nm (a) before irradiation (b) stationary concentration under irradiation at 313 nm. Column C18, eluent methanol/water, 55/45 (water with TBA 10^{-2} mol l^{-1}).

4. Direct photolysis

Before studying the photocatalytic transformation it is useful to study the direct photolysis in the absence of catalyst. Aqueous solutions of *trans*-DSD (2×10^{-5} mol l^{-1}) were exposed to the UV light with a lamp emitting between 300 and 450 nm. Solutions were analyzed in HPLC to follow the DSD concentration. In a first step, the wavelength of detection was fixed to 357 nm in accordance with the maximum absorption of the *trans*-DSD. Kinetics of DSD consumption is shown in Fig. 5. Initially, a significant decrease of DSD is observed in good agreement with the *trans–cis* isomerisation. Then, when photostationary state is reached, photolysis takes place corresponding to the slow consumption of DSD that corresponds to the second part of the graph. The quantification of photolysis was not easy in

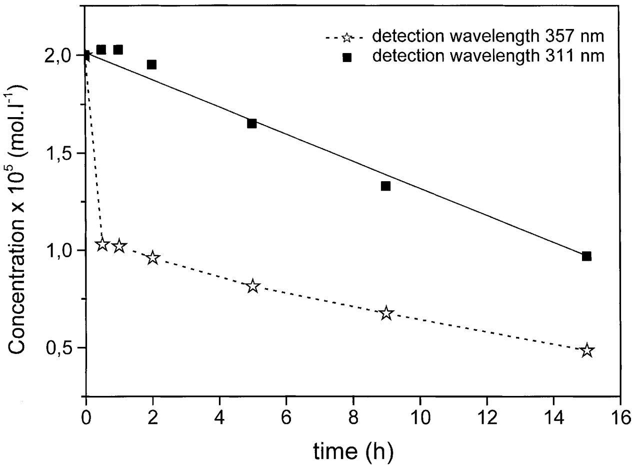


Fig. 5. Kinetics of direct photolysis of DSD (2×10^{-5} mol l^{-1}) irradiated in the range 300–450 nm.

these conditions because of the superposition of *trans* → *cis* isomerisation and photolysis phenomena, consequently experiments were repeated using detection wavelength at the isosbestic point (311 nm). In these conditions both forms have the same molar absorption coefficient and the disappearance can be directly deduced from the decrease of HPLC peak.

This method was used to measure the quantum yield of disappearance at low conversion extent in aerated aqueous solutions irradiated at 313 and 365 nm. Quantum yield was evaluated at 2.2×10^{-4} and 2.4×10^{-4} at these two wavelengths, respectively, which is in good agreement with data reported in literature [13].

5. Photocatalysis

5.1. TiO_2 slurries

Solutions of DSD 2×10^{-5} mol l^{-1} were irradiated in the presence of various catalysts in slurry or immobilized on inorganic supports. Disappearance was measured by HPLC with UV detection. A solution without catalyst was irradiated in the same conditions. When detection is set at 350 nm a rapid decrease is noted during the first minutes for the solution with the catalyst. Afterwards this decrease is much slower as it was observed in direct photolysis. The initial rapid decrease does not appear when detection is set at the isosbestic point (311 nm) (Fig. 6) and hence, this decrease is attributed to photoisomerisation. When the solution is irradiated in the presence of TiO_2 2 g l^{-1} the total disappearance is obtained after 30 min with P25 and approximately 70 min with PC50. This disappearance is easier to differentiate from photoisomerisation when the detection wavelength is set at 311 nm. The formation of a main photoproduct with shorter retention time was observed with P25. Its identification is in progress. With PC50 the reaction is less rapid and less specific. For this reason P25 was used to impregnate porous supports.

5.2. Immobilization of TiO_2

TiO_2 immobilized by sol–gel dip-coating technique on red brick or white cement and by impregnation technique of pumice stone or Volvic lava as described in Section 2.3 was used for the photocatalytic transformation of DSD. It appears on Fig. 7 that degradation of DSD is less rapid

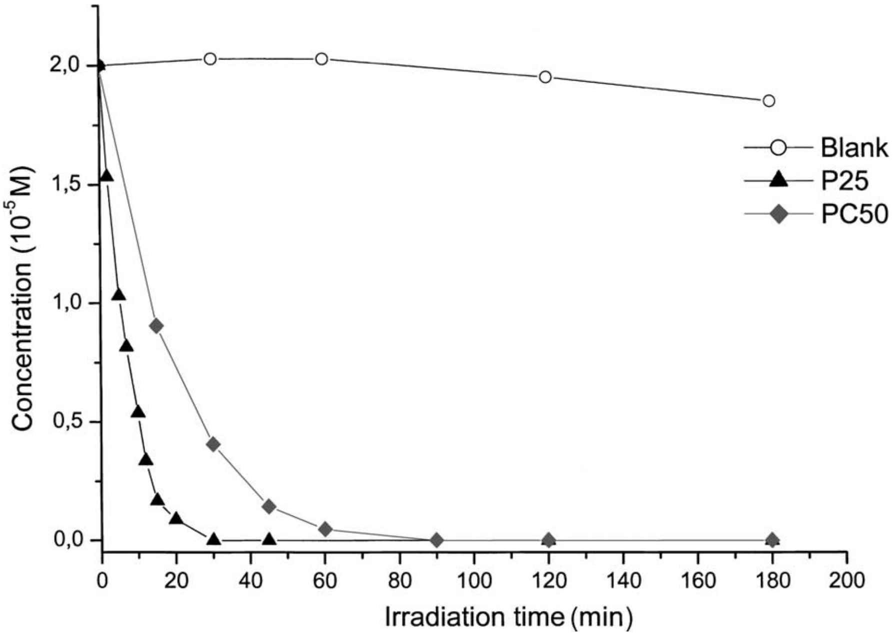


Fig. 6. Photocatalytic transformation of DSD 2×10^{-5} mol l^{-1} with TiO_2 Degussa and Millennium PC50 (detection at 311 nm).

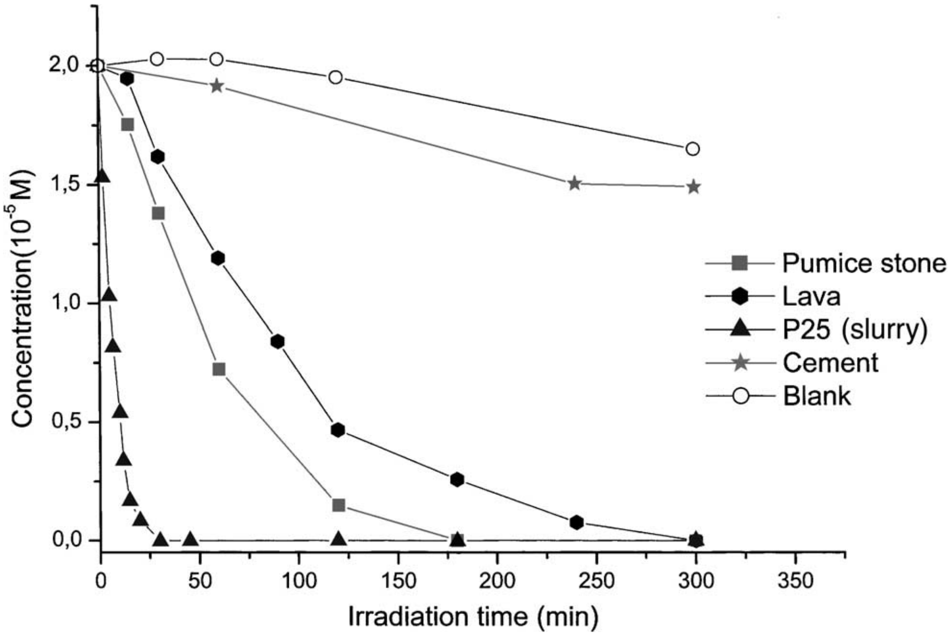


Fig. 7. Photocatalytic transformation of DSD 2×10^{-5} mol l^{-1} with TiO_2 in slurry (triangles) on various supports (analysis by HPLC, UV detection at 311 nm).

than with slurry. It is much more rapid with impregnated pumice stone and Volvic lava than with deposition of TiO_2 by sol–gel dip-coating method on white cement (similar results were obtained with red bricks) in spite of a smaller surface exposed (22, 16 and 13.2 cm^2 for cement, pumice stone and Volvic lava, respectively). These results are encouraging for the use of porous lavas as support of photocatalyst as it was recently pointed out for the transformation of other nitrobenzenesulfonic derivatives [16].

6. Conclusions

Photoisomerisation is the main photochemical process when solutions of DSD are irradiated in UV range. This phenomenon may be observed by spectrophotometry or by HPLC but the determination of the UV spectrum of *cis* form is easier by coupling both the methods. Quantum yields were evaluated at 0.30 and 0.24, respectively for *trans* → *cis* and *cis* → *trans* transformations.

At wavelengths longer than 311 nm *cis* is less absorbing than *trans* form, particularly at $\lambda > 340$ nm. To prevent from mis-interpretation of the decrease of absorbance in the study of photolysis or photocatalytic transformation when UV detection is used, it is recommended to detect at the isosbestic point(s) (311 nm in the present case).

The quantum yield of photolysis is quite low [2.2×10^{-4} to 2.4×10^{-4}] that is consistent with the deactivation of the excited states via isomerisation. Then photocatalysis may accelerate the elimination DSD from polluted waters. With TiO_2 in slurry Degussa P25 is more efficient than Millennium PC50. Immobilization of TiO_2 significantly reduces its efficiency, but encouraging results were obtained using TiO_2 on porous supports and in particular with pumice stone which has a good retention for TiO_2.

Acknowledgements

This work was supported for a large part by Indian–French Centre for Advanced Research (IFCPAR contract 2205.2). The authors are grateful to Dr Chantal Guillard for her skillful assistance for sol–gel dip-coating. They are indebted to Millennium Inorganic Chemicals for providing TiO_2 PC50.

References

[1] T. Poiger, J.A. Field, T.M. Field, W. Gieger, Anal. Meth. Instrum. 1 (1993) 104.
[2] Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, A3, 1991 p. 255.
[3] P. Wong-Wah-Chung, Thesis of Université Blaise Pascal, France, December 2001.
[4] J. Saltiel, J. Am. Chem. Soc. 89 (1967) 1036.
[5] J. Saltiel, J. D'Agostino, E.D. Megarity, L. Metts, K.R. Neuberger, M. Wrighton, O.C. Zafiriou, in: O.L. Chapman (Ed.), Organic Photochem, Vol. 3, Marcel Dekker, New York, 1973.
[6] J. Saltiel, J.L. Charlton, in: Mayo (Ed.), Rearrangement in Ground and Excited States, Vol. 3 Academic press, New York, 1980.
[7] D.H. Waldeck, Chem. Rev. 91 (1991) 415.
[8] V. Papper, D. Pines, G. Likhtenshtein, E. Pines, J. Photochem. Photobiol. A: Chem. 111 (1997) 87.
[9] V. Papper, G.I. Likhtenshtein, J. Photochem. Photobiol. A: Chem. 140 (2001) 39.
[10] S. Canonica, J.B. Kramer, D. Reiss, H. Gygax, Environ. Sci. Technol. 31 (1997) 1754.

[11] S. Husain, R. Narshimha, S.N. Alvi, N.R. Rao, J. Chromatogr. 596 (1992) 127.

[12] P. Wong-Wah-Chung, G. Mailhot, M. Bolte, J. Photochem. Photobiol. A: Chem. 138 (2001) 275.

[13] J.B. Kramer, S. Canonica, J. Hoigné, J. Kaschig, Environ. Sci. Technol. 30 (1996) 2227.

[14] A. Rachel, M. Subrahmanyam, P. Boule, Appl. Catal. B: Environ. 37 (2002) 301.

[15] E. Fischer, J. Phys. Chem. 61 (1967) 3704.

[16] A. Rachel, B. Lavédrine, M. Subrahmanyam, P. Boule, Catal. Comm. 3 (2002) 165.