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# Irradiation-wavelength dependent photochemistry of the bichromophoric sulfonylurea chlorsulfuron

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## Abstract

The photochemistry of the bichromophoric sulfonylurea chlorsulfuron has been investigated at different irradiation wavelengths and environmental conditions. The identified products indicate that different reaction paths are followed, depending whether the benzene or the triazine component chromophores are excited. In the first case, the chlorine atom is substituted by hydrogen or hydroxyl in water; in the second one three competitive photodegradation paths may be followed, the most efficient one being the cleavage of the S–N bond in the sulfonylurea bridge. Photodegradation quantum yield measurements, combined with laser flash photolysis experiments have shown that, while both singlet and triplet states contribute to all photolytic paths in deaerated solution, quenching by oxygen makes the triplet contribution negligible in samples equilibrated with air. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Bichromophoric compounds; Photolysis; Chlorsulfuron; Sulfonylureas

## 1. Introduction

The photophysics and photochemistry of multichromophoric systems have been the subject of intensive study in the last decades [1]. In many instances, the central question is the extent and nature of the interchromophore interaction: this determines phenomena of both basic and applicative interest, such as exciton coupling, optical electron transfer, photoinduced energy and electron transfer, wavelength-dependent photochemistry. An example of a family of bichromophoric compounds is provided by substituted sulfonylureas with general formula X–$SO_2$–$NR_1$–CO–$NR_2$–Y, where X is an unsaturated cycle (e.g., benzene, pyridine, thiophene), Y is an *N*-heterocycle (triazine or pyrimidine) and $R_{1,2}$ are usually hydrogen atoms: here, the main components of the two photoactive chromophores are the terminal unsaturated cycles. These compounds are very potent herbicides whose persistence in soil is crucial to their use [2]. The main degradation paths are microbial metabolization and hydrolysis, but photodegradation caused by the sunlight can affect the persistence, depending on the quantum yield of the process and the overlap of the absorption of the compound with the solar spectrum.

Reports on the photochemistry of sulfonylureas are scanty and never pointed out their bichromophoric nature and its consequence on reactivity. Aryl butyl sulfonylureas were shown to undergo, upon irradiation, a homolytic cleavage of the S–N bond in non-aqueous solvents [3]. Some photocleavage of the C–S bond was proposed to occur too. Closer to the problem of our interest is a study of the photolysis of the sulfometuron methyl in water [4]. The authors of that study could only identify two of the several photoproducts observed; these likely resulted from the two previously mentioned photocleavages. For none of the photoreactions investigated were quantum-yield values reported.

In this contribution we present a study of the photochemistry of chlorsulfuron (2-chloro-*N*[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-aminocarbonyl]benzenesulfonamide, CLS, see Scheme 1) in an aqueous environment. As we shall see, CLS contains two weakly coupled chromophores, namely, substituted benzene and s-triazine. As a result of this, it exhibits an excitation-wavelength dependent photochemistry. The nature of the main photoproducts obtained upon irradiation of both its neutral and anionic forms at two different wavelengths in the near-UV region has been determined. While excitation of the benzene-like chromophore leads to chlorine elimination or substitution, absorption by the triazine chromophore results in energy transfer to the sulfonylurea bridge and subsequent competitive cleavage reactions. Quantitative information on the mechanism of photodegradation has been obtained from measurements of its quantum yield at two different excitation wavelengths, corresponding to selective excitations of the two chromophores and at

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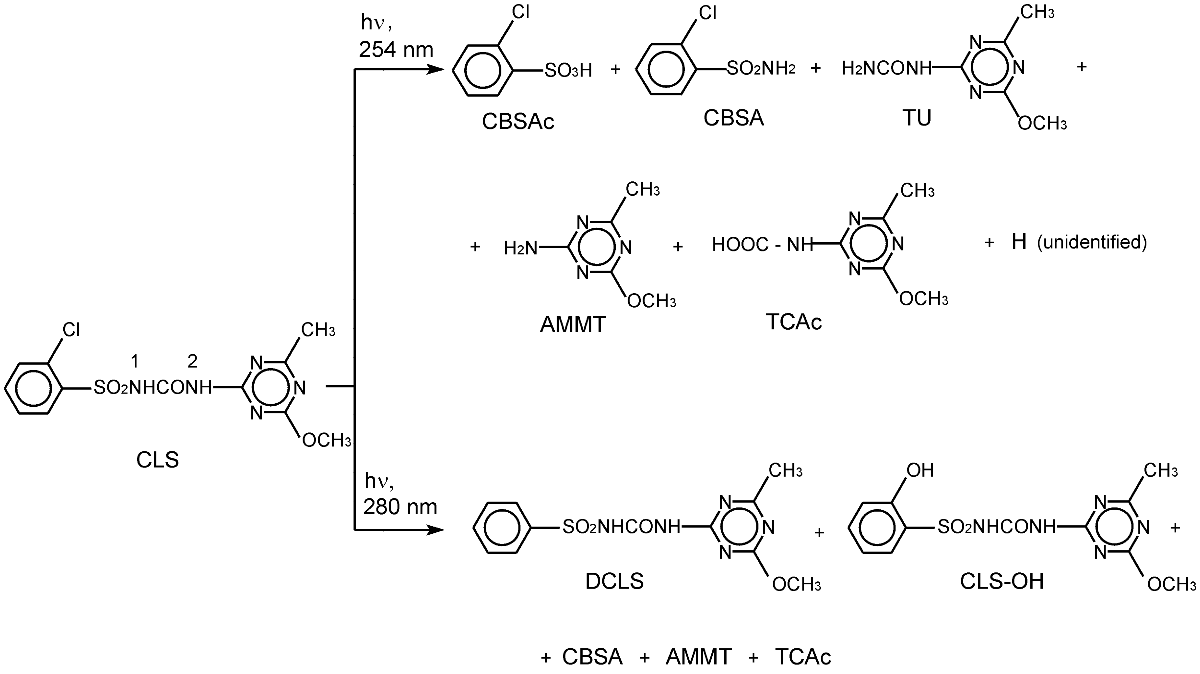


Scheme 1.

different values of pH and oxygen concentration. Laser flash photolysis experiments have provided kinetic information about the lowest triplet state. Finally, we have explored the photobehaviour of CLS in conditions closer to the natural ones by irradiating it with a solar simulator.

## 2. Experimental details

### 2.1. Materials and instrumentation

CLS was an analytically certified sample from Dr. Ehrensdorfer GmbH and was used as received. Deionized water, acidified with hydrochloric or orthophosphoric acid and acetonitrile (Labscan, HPLC grade) were used as the solvents. Deaeration of the samples, obtained by performing three freeze-pump-thaw cycles, preceded equilibration with different oxygen pressures. Deuterated chloroform (Aldrich and Isotec) was treated with activated molecular sieves to remove traces of water before the $^1$H-NMR measurements. Absorption spectra were recorded on a Perkin Elmer λ15 UV–Vis spectrophotometer. High pressure liquid chromatography was performed with an HP series 1050 instrument equipped with a UV diode-array detector (HPLC–UV) and a Hypersil ODS 5 μm column. A 7:3 (v/v) water (pH 2.7)–acetonitrile mixture was used as the eluent at a constant 1 ml/min flow rate. Proton NMR spectra were measured on a Bruker AMX 200 MHz FT-NMR spectrometer at 300 K using standard pulse sequences and instrumental parameters. Electronic ionisation mass spectra were obtained from a Finnigan MAT SSQ 710A spectrometer, using a probe for direct introduction of solid samples. A PESCIEX ionspray single-quadrupole mass spectrometer (model API 150 EX) with positive ion detection and sample cone voltage optimized at 37 V to increase sensitivity while decreasing ion fragmentation, was employed to analyse the photolysed solutions and confirm the identification of several photoproducts.

### 2.2. Hydrolysis

According to the literature [5,6], hydrolysis of CLS follows two competitive paths with comparable rates in acidic solution: these involve, respectively, the sulfonylurea bridge, eventually yielding 2-chloro-benzenesulfonamide and 2-amino-4-methoxy-6-methyl-1,3,5-triazine and the 4-methoxy substituent at the triazine ring, yielding the 4-hydroxy derivative. We have carried out hydrolysis experiments to help at identifying the first two compounds among the photoproducts and estimate their amounts. CLS was hydrolysed in water in the dark at pH 4 and $T = 60°C$ and at pH 2.5 and $T = 35°C$. The products were analysed by HPLC–UV in the same conditions as were employed with photolysis (see below). Their assignments were straightforward, based on the results in Ref. [5,6].

### 2.3. Photolysis

CLS in its neutral form is only sparely soluble in water. Its solubility, however, increases rapidly upon addition of an organic solvent. We have therefore investigated its photodegradation in a water–acetonitrile 7:3 (v/v) mixture.

Once the main aspects of CLS photodegradation had been understood, photolysis was also carried out in water at pH 2, 4, 6 and 8. Most quantitative experiments were carried out at room temperature (ca. 20°C) by irradiating solutions of CLS with a low-pressure mercury-arc lamp ($\lambda_{\mathrm{irr}} = 254\,\mathrm{nm}$). Photodegradation was significant (20–30%) after 1–2 h, a time during which hydrolysis was irrelevant at all pH values adopted. The samples had concentrations between $1 \times 10^{-4}$ and $5\times10^{-4}\,\mathrm{mol\,l^{-1}}$. Photodegradation quantum yields were determined as follows. The concentration of residual CLS at a given irradiation time was evaluated from the area of the peak measured by HPLC–UV using a calibration factor obtained from the area of the peak of a non-irradiated sample of known concentration. Residual CLS concentrations were plotted versus irradiation time. The slope at the origin of such a plot gave the initial rate of photodegradation. The quantum yield was obtained by dividing this rate by the rate of photon absorption, determined in the same geometrical conditions with a *trans*-azobenzene actinometer [7]. Total absorption of the 254 nm light by the CLS samples was ensured in all cases. An estimate of the concentrations of the two products also formed in hydrolysis was obtained as follows. From the areas of the chromatographic peaks, *A*, the concentration of a photoproduct P at a given irradiation time *t* was determined in terms of the concentration of residual CLS as

$$C_{\mathrm{P}}(t) = \frac{A_{\mathrm{P}}}{A_{\mathrm{CLS}}}\frac{\varepsilon_{\mathrm{CLS}}}{\varepsilon_{\mathrm{P}}}C_{\mathrm{CLS}}(t) \qquad (1)$$

where $\varepsilon$ are the molar extinction coefficients averaged over the spectral window of the HPLC detector, 240 ± 15 nm. The extinction coefficient ratios necessary to apply the previous equation were determined through hydrolysis experiments, knowing the relative efficiencies of the two mentioned hydrolytic routes in our experimental conditions [5,6] and applying simple mass balance considerations.

Irradiation of CLS was also carried out at several other wavelengths, selected either from a medium-pressure mercury lamp with an interference filter (270 nm) or by using the excitation compartment of a fluorometer (245 and 280 nm with 10 and 6 nm slit widths). Finally, photolysis with a solar spectrum lamp was carried out at about 30°C on $2 \times 10^{-4}$–$3 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$ solutions of CLS in water (pH 2.6 and pH 6)–acetonitrile 7:3 (v/v) mixtures equilibrated with air.

### 2.4. Product analysis

To identify the main photoproducts, samples that had been degraded to about 40–50% of the initial concentration upon irradiation at 254 nm were analysed by HPLC–UV. The main fractions were then collected in 5–6 subsequent runs. The solvent was evaporated and the solid residues were analysed via mass spectrometry or recovered with deuterated chloroform for NMR spectral characterisation. Samples irradiated at 280 nm contained lower concentrations of products and were analysed via HPLC–UV. The identities of the compounds obtained at both irradiation wavelengths were confirmed via liquid-chromatography/ionspray mass spectrometry with positive ion determination and low fragmentation efficiency. The main products found and the chromatographic, UV, $^1$H-NMR and mass spectrometric data used for their identification are given below. Their structures are shown in Scheme 1.

*Product A*: 2-chloro-benzenesulfonic acid (CBSAc). HPLC retention time ($t_{\mathrm{r}}$): 0.9 min (tail of broader peak) ($t_{\mathrm{r}} = 0.8$ min for benzenesulfonic acid in the same conditions); UV maxima ($\lambda_{\max}$): 217, 276 nm (structured benzene $\mathrm{L_b}$-like band, $\lambda_{\max} = 264$ nm for benzenesulfonic acid); $^1$H-NMR: 8.1 ppm (dd, 1H) and 7.2–7.5 ppm (multiplet, ∼3H); mass spectrum (MS): 194 (31), 192 (100, $\mathrm{M^+}$), 174 (35), 128 (95, $\mathrm{M^+{-}SO_2}$), 111 (32), 97 (32), 75 (35) (relative peak intensities are given in parentheses).

*Product B*: 2-chloro-benzenesulfonamide (CBSA). $t_{\mathrm{r}} = 2.4$ min. UV: $\lambda_{\max} = 219$, 272 nm (structured benzene $\mathrm{L_b}$-like band). $^1$H-NMR: 8.15 ppm (dd, 1H), 7.4–7.6 ppm (multiplet, ∼3H), 5.1 ppm (bs, 2H, assigned to the sulfonamide $\mathrm{NH_2}$ protons [8]); MS: $m/e = 193$ (35), 191 (100, $\mathrm{M^+}$), 128 (52), 127 (52, $\mathrm{M^+{-}SO_2}$), 111 (98, $\mathrm{M^+{-}SO_2NH_2}$), 75 (70). Ionspray mass spectrum (IMS): $m$ ($\mathrm{M{-}H^+}$) = 192 (100), 194 (30). It was also a hydrolysis product.

*Product C*: *N*[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-aminocarbonyl]benzenesulfonamide (dechlorinated CLS, DCLS). $t_{\mathrm{r}} = 4.7$ min (it is eluted shortly before residual CLS). UV: exhibits both the benzene $\mathrm{L_b}$-type band structure ($\lambda_{\max} = 264$ nm, $\lambda_{\max} = 272$ nm for CLS) and the triazine centred band around 240 nm. IMS: $m$ ($\mathrm{M{-}H^+}$) = 324.

*Product D*: 2-hydroxy-*N*[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-aminocarbonyl] benzenesulfonamide (CLS-OH). $t_{\mathrm{r}} = 3$ min. UV: $\lambda_{\max} = 221$, 286 nm (blurred vibronic structure, similar to that exhibited by 2- [9] and 3-hydroxy-benzenesulfonamide [10]); ca. 245 nm (triazine-like shoulder). IMS: $m$ ($\mathrm{M{-}H^+}$) = 340.

*Product E*: 2-amino-4-methoxy-6-methyl-1,3,5-triazine (AMMT, positively identified by comparison with an authentic sample). $t_{\mathrm{r}} = 4.4$–4.5 min. UV: only triazine-like absorption ($\lambda_{\max} = 216$ nm, shoulder at 245 nm). $^1$H-NMR: 5.2 ppm (bs, 2H, $\mathrm{NH_2}$), 3.95 ppm (s, 3H, $\mathrm{OCH_3}$), 2.41 ppm (s, 3H, $\mathrm{CH_3}$). MS: $m/e = 140$ (100, $\mathrm{M^+}$), 110 (63, $\mathrm{M^+{-}OCH_3{+}H}$), 69 (72), 42 (50). IMS: $m$ ($\mathrm{M{-}H^+}$) = 142. It is also one of the main products of hydrolysis.

*Product F*: *N*-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-urea (TU). $t_{\mathrm{r}} = 1.41$ min. UV: $\lambda_{\max} = 245$ nm (single-band spectrum). MS: $m/e = 183$ (35, $\mathrm{M^+}$), 140 (100, $\mathrm{M^+{-}HNCO}$), 110 (45), 69 (45). $^1$H-NMR: $\delta = 4.02$ ppm (s, 3H), 2.5 ppm (s, 3H), intermediate between those of CLS and AMMT. IMS: $m$ ($\mathrm{M{-}H^+}$) = 184.

*Product G*: suggested identification (4-methoxy-6-methyl-1,3,5-triazin-2-yl)-carbamic acid (TCAc). $t_{\mathrm{r}} = 0.9$ min (front of broader peak). UV: $\lambda_{\max} = 222$ nm; shoulder at ca. 245 nm. $^1$H-NMR: $\delta \approx 4$ ppm (s), 2.5 ppm (s), very noisy. IMS: $m$ ($\mathrm{M{-}H^+}$) = 185.

*Product H*: unidentified triazine derivative. $t_r = 1.46$ min. UV: $\lambda_{max} = 222$ nm; shoulder at ca. 245 nm. $^1$H-NMR: $\delta \approx$ 4 ppm (s), 2.5 ppm (s), very noisy.

### 2.5. Laser flash photolysis

The fourth harmonic of a Quantel YG585 Nd-YAG laser (266 nm, 10 ns, ca. 5 mJ) was used for excitation. The transient absorption curves were fed into a Tektronix TDS 520 digital-storage oscilloscope and analysed by standard computer programs. In order to improve the signal-to-noise ratios, the transient-absorption profiles were digitally smoothed and averaged over 10–30 repetitions.

## 3. Results

### 3.1. Absorption spectrum and acid–base equilibria

The bichromophoric nature of CLS is demonstrated by its absorption spectrum, shown in Fig. 1 together with the spectra of 2-chloro-benzenesulfonamide (CBSA) and 2-amino-4-methoxy-6-methyl-1,3,5-triazine (AMMT), which are representative of the two chromophoric components of CLS. In the wavelength region reported, the spectrum of CLS shows three significant features: the structured benzene-like $L_b$-type band, shifted by about 4 nm to the red with respect to the corresponding band of CBSA; the triazine-centred shoulder between 240 and 260 nm, exhibited by AMMT as well; and the band with maximum at 222 nm, slightly red-shifted with respect to the most intense bands of the two component chromophores. The urea-centred electronic transitions lie at higher energies [11]. The absence of new peculiar bands and the small spectral shifts observed suggest that weak interactions take place among the electronic systems of the two chromophores and of the sulfonylurea connecting bridge. A more quantitative assessment of such interactions in this and other sulfonylureas is under way.

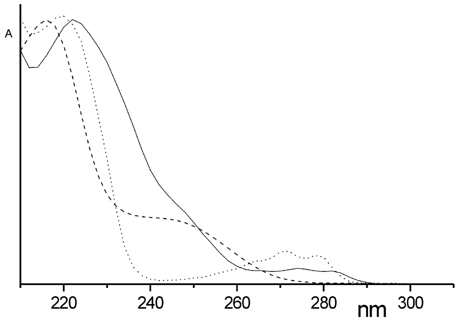


Fig. 1. Normalised absorption spectra of CLS (—), CBSA (· · ·) and AMMT (–) in a water (pH 2.6)–acetonitrile 7:3 (v/v) mixture (the spectra were obtained in the HPLC–UV analysis of hydrolysis experiments; see Section 2 for details).

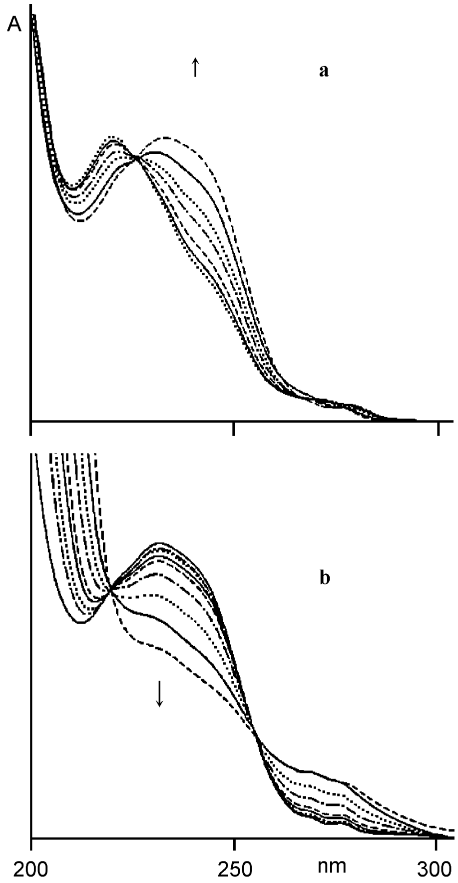


Fig. 2. Dependence on pH of the electronic absorption spectrum of CLS in water ($7 \times 10^{-5}$ mol l$^{-1}$). pH ranges: (a) 2.97 (· · ·)–6.46 (–); (b) 11.05 (—)–13.29 (–). Arrows indicate the effect of increasing pH.

The spectrum of CLS in water changes with pH as shown in Fig. 2a and b. The change is reversible upon inversion of pH and reflects the two acid–base equilibria in which CLS is involved in the 1–14 pH range. Calculations of the two p*K*s were performed at several wavelengths, according to the usual analysis of absorbance data [12]. They yielded $pK_1 = 3.7 \pm 0.15$ and $pK_2 = 13.1 \pm 0.2$. The monoanion is therefore the dominant form of CLS in the aqueous phase of most soils; only in acidic environments is a significant amount of the neutral form expected.

### 3.2. Photolysis

Irradiation with a low-pressure mercury-arc lamp ($\lambda_{irr} =$ 254 nm) of neutral and monoanionic CLS solutions in air-equilibrated acetonitrile–water 3:7 (v/v) mixtures caused, in few tens of minutes, pronounced spectral changes, such as those shown in Fig. 3a and b. Fairly good isosbestic points, occurring at 250 nm in Fig. 3a and at 223 and 264 nm in Fig. 3b, were preserved for times corresponding to the disappearance of about 40–50% of the initial amount. They were slowly missed upon further irradiation. Comparison of Fig. 3a and b shows that, although the initial spectra

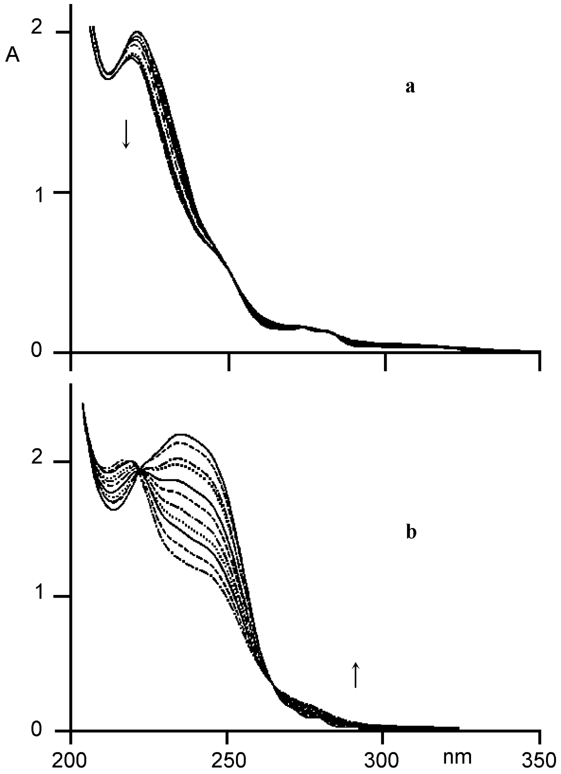


Fig. 3. Changes in the absorption spectra of neutral (a) and monoanionic (b) CLS in acetonitrile–water ((a) pH 2.6; (b) pH 6.6) 3:7 (v/v) mixture caused by irradiation at 254 nm. Initial concentrations were $4.4 \times 10^{-4}$ (a) and $4.6 \times 10^{-4}$ mol $l^{-1}$ (b). The optical path was 2 mm. Total irradiation times were approximately 3 (a) and 1.5 h (b).

of neutral and anionic CLS were well differentiated from each other, photolysis caused changes that resulted in quite similar “final” spectra. Indeed, HPLC–UV analysis of the irradiated samples showed that UV photolysis of neutral and anionic CLS yielded the same main products. These are shown in the upper part of Scheme 1. The analytical details leading to their identification are given in Section 2.

The time evolution of the main products obtained at $\lambda_{irr} = 254$ nm is shown in Fig. 4, where the areas of the corresponding chromatographic peaks, each normalised to its maximum value, are reported as functions of the irradiation time. All of them increase roughly parallelly with the only exception of DCLS which rapidly reaches a maximum and then slowly decreases. The latter, however, was obtained in very low amounts at this irradiation wavelength. This indicates that, as long as CLS absorbed most of the lamp light, photoproducts were formed in constant ratios according to a competitive-reaction scheme, in keeping with the observation of isosbestic points in the UV spectra of Fig. 3a and b.

A quantitative determination of photoproducts CBSA and AMMT was obtained through Eq. (1): 20–25% of photolysed neutral CLS was recovered as CBSA, while an even lower amount, of the order of 10%, was obtained from anionic CLS. On the other hand, AMMT was recovered as 50–70% of photolysed neutral CLS and about 30% of anionic CLS. So, the two products were formed in, roughly, a 1:3 mole ratio.

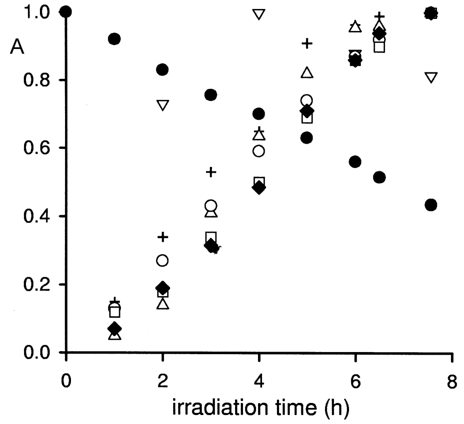


Fig. 4. Areas of the HPLC peaks of the main photoproducts of neutral CLS as functions of the irradiation time (the areas have been normalised to their maximum values): (●) CLS; (○) CBSAc + G; (□) TU; (◆) H; (+) CBSA; (△) AMMT; (▽) DCLS.

To test the consequence of the bichromophoric character of CLS on its photoreactivity, we have compared the natures and relative amounts of photoproducts obtained from its neutral form in the aerated binary solvent mixture at four irradiation wavelengths, namely, 245 (±5), 254 (±2), 270 (±2) and 280 (±3) nm. Along this series, excitation progressively shifts from the triazine to the benzene chromophore. The most important change observed concerned the relative yields of formation of DCLS on one hand and of CBSA and AMMT, on the other. These were determined from the slopes of plots of the areas of the corresponding peaks versus the areas of the residual CLS peaks measured at different irradiation times. Inspection of the results reported in Table 1 reveals that dechlorination of CLS is negligible when the excitation is centred on the triazine chromophore (245 and 254 nm), while it becomes much more relevant upon excitation of the benzene chromophore (270 and 280 nm). On the other hand, CBSA and AMMT result preferentially from excitation of triazine, even though they were still obtained with significant yields upon irradiation at 280 nm. Photolysis at this wavelength also caused the appearance of the photosubstitution product CLS-OH (lower part of Scheme 1). In

Table 1
Dependence of the relative formation yields of some products on the irradiation wavelength ($\lambda_{irr}$)[a]

| $\lambda_{irr}$ (nm) | DCLS[b] | CBSA[c] | AMMT[d] |
|---|---|---|---|
| 245 ± 10 | 0.02 | 0.06 | 0.19 |
| 254 ± 2 | 0.05 | 0.06 | 0.18 |
| 270 ± 3 | 0.25 | ≈0 | ≈0 |
| 280 ± 10 | 0.35 | 0.01–0.02 | <0.08 |

[a] The meaning of the reported figures is given in the text.

[b] Dechlorinated CLS.

[c] 2-Chlorobenzenesulfonamide.

[d] 2-Amino-4-methoxy-6-methyl-1,3,5-triazine.

view of the strong similarity of the absorption spectra of this compound, CLS and DCLS in the 210–260 nm region, we may assume that they have similar $\varepsilon$ values at $240 \pm 15$ nm. Under this assumption, we find that DCLS and CLS-OH are formed at similar rates and, together, account for more than half of the CLS disappeared in these experimental conditions.

Photolysis at 254 nm of anionic CLS in the aerated binary mixture, of neutral CLS in acetonitrile and of both forms in the deaerated solvent mixture yielded essentially the main photoproducts already described, though in modified relative amounts. So, the triazine derivative G, likely TCAc, was hardly observable in the photolysis of anionic CLS. On the other hand, in acetonitrile, neither CBSAc nor TCAc nor CLS-OH were obtained, while DCLS was formed in a much larger amount than in the binary mixture.

DCLS, CLS-OH, CBSAc, TU, TCAc and H were the compounds obtained in significant amounts in the photolysis of both neutral and anionic CLS in the water–acetonitrile mixture using a solar simulator. Their quantitative distribution was similar to that observed upon preferential excitation of the benzene chromophore. Indeed, this was expected since the spectrum of this source overlapped much better with the benzene $L_b$-type band than with the triazine-centred band of CLS.

### 3.3. Mechanistic aspects

Information about the photodegradation quantum yield of CLS ($\Phi$) and its dependence on the environment (solvent, pH, oxygen concentration) and the irradiation wavelength is provided by the data collected in Table 2. They reveal a marked increase of $\Phi$ with decreasing pH at $\lambda_{irr} = 254$ nm. Such a behaviour is likely determined by the position of the first acid–base equilibrium of CLS at different pH values and the higher quantum yield of the neutral relative to the anionic forms in water. A decrease in quantum yield, from ca. $5 \times 10^{-2}$ to $1.5 \times 10^{-2}$, was found for neutral CLS on moving from water to acetonitrile. A slightly lower value, $0.9 \times 10^{-2}$, was measured in the binary mixture. Here, contrary to what found in water, anionic CLS had essentially the same quantum yield, $1 \times 10^{-2}$ (not reported in Table 2), as neutral CLS. The similarity of $\Phi$ in acetonitrile and in the water–acetonitrile mixture and its higher value in water at pH 2 suggest preferential solvation of neutral CLS by the organic solvent in the binary mixture, consistently with its very low solubility in water at pH lower than p$K_1$.

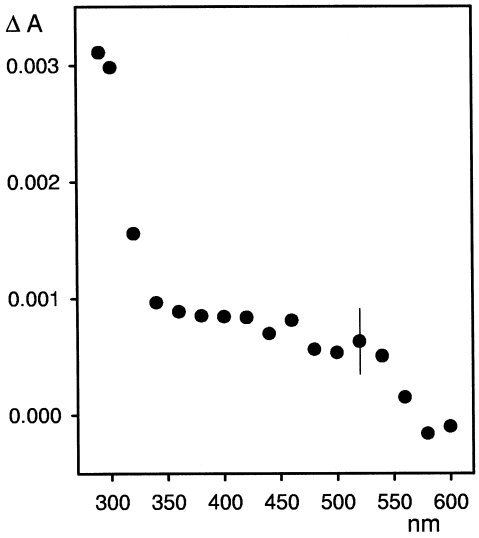


Fig. 5. Differential absorption spectrum of a deaerated sample of neutral CLS in a water (pH 2.6)–acetonitrile 7:3 (v/v) mixture, measured 600 ns after laser excitation at 266 nm. A representative error bar is shown.

The important changes brought about by a shift in the irradiation wavelength from 254 to 280 nm also included the photodegradation quantum yield. This was about 3.5 times larger when irradiating at the longer wavelength: the benzene chromophore is more reactive than the triazine chromophore.

The photodegradation quantum yields of neutral CLS at both wavelengths decreased with increasing oxygen pressures (Table 2). The effect was already significant at 0.23 atm, corresponding to an oxygen concentration of $3 \times 10^{-4}$ mol l$^{-1}$. We assume this to indicate that both singlet and triplet states are involved in these photoreactions in deaerated solutions. Interestingly, only the formation of CLS-OH, among all products observed, was not quenched by oxygen in the air-equilibrated solution.

Very low transient absorption signals were observed upon laser excitation at 266 nm of neutral CLS in the water–acetonitrile mixture (Fig. 5). The differential spectrum consists of a broad, diffuse absorption extending between 350 and 580 nm and the onset of a more intense band between 300 and 350 nm. We could only discriminate a single transient: its decay was monoexponential and much the

Table 2
Photodegradation quantum yields ($10^2\Phi$) of CLS

| $\lambda_{irr}$ (nm) | Solvent | $p_{O_2} = 0$[a] | 0.23 atm | 1.5 atm |
|---|---|---|---|---|
| 254 | $H_2O$ | | 5.0 (pH 2), 2.5 (pH 4), 2.0 (pH 6), 1.9 (pH 8) | |
| 254 | $CH_3CN$ | | 1.5 | |
| 254 | $H_2O$–$CH_3CN$ 3:1[b] | 1.1 | 0.9 | 0.6 |
| 280 | $H_2O$–$CH_3CN$ 3:1[b] | 5.2 | 3.5 | |

[a] Oxygen pressure in equilibrium with the samples ($p_{O_2} = 0.23$ atm corresponds to air).

[b] Neutral CLS.

Table 3
Lifetime ($\tau$) of the transient species observed in the laser flash photolysis of neutral CLS in the water–acetonitrile mixture

| | | | | | |
|---|---|---|---|---|---|
| $p_{O_2}$ (atm) | 0 | 0.23 | 0.25 | 0.5 | 1.0 |
| $\lvert O_2 \rvert$ ($10^4$ mol l$^{-1}$)[a] | 0 | 3.0 | 3.2 | 6.5 | 12.9 |
| $\tau$ ($10^{-6}$ s) | 2.7 | 0.8 | 1.1 | 0.5 | 0.25 |

[a] Calculated from $p_{O_2}$ values using the Bunsen absorption coefficient in water, $\alpha = 0.029$ [13].

same at all wavelengths. A very weak longer-lived absorption appeared at 300–310 nm. The lifetime decreased with increasing oxygen concentration as reported in Table 3: analysis of the data yielded a bimolecular quenching constant $k_{O_2} = (2.5 \pm 0.5) \times 10^9\,\text{mol}^{-1}\,\text{l}\,\text{s}^{-1}$, consistent with a diffusional quenching. In the same air-equilibrated solvent mixture, we measured the triplet lifetime of eosin Y and obtained a similar result: $\tau = 1.1 \pm 0.2\,\mu\text{s}$. We assign the observed transient as the $T_1 \rightarrow T_n$ absorption of CLS, also consistently with the similarity of its spectrum with the $T_1 \rightarrow T_n$ spectra exhibited, in the wavelength region accessible to our experiments, by benzene [14], some of its mono and disubstituted derivatives [15,16] and s-triazine [17], i.e., the constituent chromophores of CLS.

A change in the oxygen concentration had a negligible effect on the differential absorbances at 410 nm evaluated at "time zero", i.e., at the maxima of the transient decay curves: these held $1.0 \times 10^{-3}$, $0.8 \times 10^{-3}$ and $\approx 0.8 \times 10^{-3}$ for oxygen pressures of 0, 0.25 and 0.5 atm, respectively. This points to inefficient quenching by oxygen at these pressures of the steps of formation of the $T_1$ state, i.e., of the $S_1$ state decay. On the other hand, the triplet state is fully quenched at 1.5 atm of oxygen ($\tau = 0.25\,\mu\text{s}$). Therefore, $6 \times 10^{-3}$ is a lower limit to the singlet-state contribution to the photodegradation quantum yield, $\Phi_S$, when exciting the triazine chromophore. So, the corresponding $\Phi_T$ will be lower than $5 \times 10^{-3}$ in deaerated solution and, since it is reduced by about three times in the air-equilibrated sample, it contributes almost negligibly to the observed quantum yield in the latter conditions. A qualitatively similar conclusion likely holds for the photolytic routes followed upon excitation of the benzene chromophore at 280 nm.

In dehydrated and deaerated acetonitrile, CLS showed the same transient absorption with the same formation efficiency as in the binary solvent mixture, therefore confirming preferential solvation by the organic solvent in the latter. The transient lifetime, $2.5 \pm 1\,\mu\text{s}$, was also similar to the lifetime in the solvent mixture. This is therefore an intrinsic value which is not determined by impurity quenching.

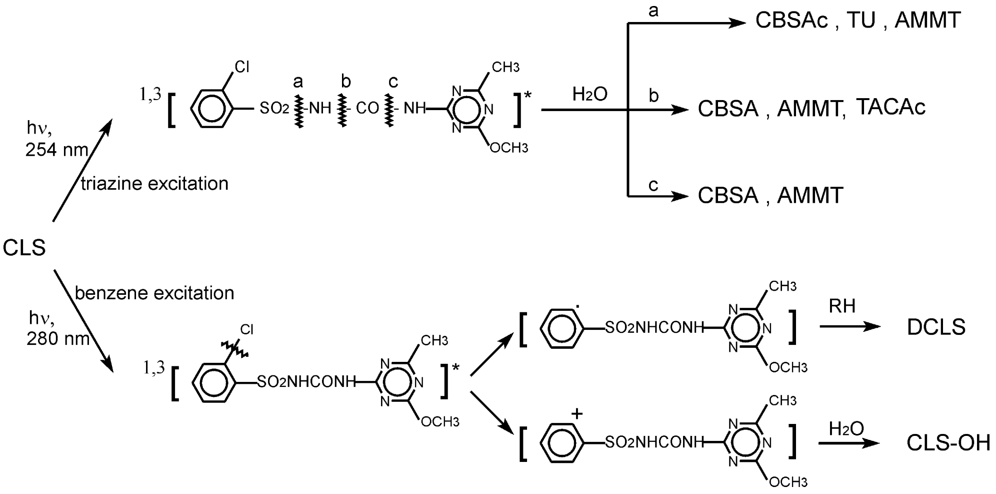
## 4. Discussion

The lowest excited, photochemically relevant states of CLS are localised in either of two chromophores centred on benzene and triazine. The benzene-centred lowest-excited singlet state lies some 35 300 cm$^{-1}$ above the $S_0$ state, corresponding to the lowest-energy absorption vibronic band. On the other hand, substituted triazine certainly contributes lower-lying n$\pi^*$ states carrying, however, very low oscillator strengths to the CLS ground state: unsubstituted s-triazine has a lowest-lying n$\pi^*$ singlet state 31 500 cm$^{-1}$ above $S_0$ [18].

On the basis of information from the literature, we can make some considerations on the nature and extension of the two chromophores. As was theoretically established by Koch and Moffitt [19] and later substantiated both spectroscopically [20] and photophysically [21], conjugation between the $\pi$ system of the aromatic ring and orbitals of the $SO_2$ group of proper symmetry is possible and weakly operative in aromatic sulfones. Also, it extends over a second aromatic $\pi$ system in diphenylsulfone derivatives, in spite of the non-coplanarity of the two benzene rings. So, in principle, conjugation between the 2-chlorobenzenesulfonyl group and the urea group in CLS might affect the energetics and decay dynamics of its excited states. However, comparison of the UV spectra of two model compounds, benzenesulfonamide and methyl-phenyl-sulfone, shows that they have superimposable $^1L_a$ and $^1L_b$ bands [20] and, therefore, that the nitrogen p electrons are essentially uncoupled with the $\pi$ system of the benzenesulfonyl group. On this basis, we propose CLS to be composed of two very weakly coupled chromophores. The first of these is 2-chlorobenzenesulfonyl. The second one certainly includes methyl-methoxy-aminotriazine; extension of conjugation to the remaining urea N(1)H–CO group, although not proved, is strongly suggested by the large change in the triazine contribution to the absorption spectrum of CLS caused by N(1)H deprotonation to form the monoanion (see Fig. 2a).

As a result of this, CLS may be thought of as consisting of two distinct molecular photoreactors: each of them conveys the energy of the absorbed photons into specific reaction paths. So, a large number of reaction products is expected and actually obtained and the observed total photodegradation quantum yield and photoproduct quantitative distribution exhibit marked changes with changing irradiation wavelength. Also, the relative rates of formation of the seven or eight products obtained by irradiating at 254 nm change with the solvent, pH and the presence or absence of oxygen. This reveals a complex mechanism with competitive paths yielding different products. Its main and soundest aspects can be outlined by combining the pieces of information collected by us and those available in the literature. Such mechanistic aspects are summarised in Scheme 2.

Chloroarenes are known to undergo photoreductive dechlorination, leading to arenes, in hydrocarbons and in some mixed water–organic solvents. On the other hand, photosubstitution is dominant in nucleophilic solvents, such as alcohols and water, yielding alkyl aryl ethers and aromatic alcohols ([22] and references cited therein). Homolytic cleavage of the C–Cl bond in the $S_1$ state, followed by hydrogen abstraction from the organic solvent is the accepted mechanism of the first reaction. Contribution from



Scheme 2.

the $T_1$ state of chlorobenzene had been excluded on the basis of simple energetic considerations [23], but it has been later proposed to occur in water–ethanol mixtures [24]. The mechanistic details of the second reaction are a subject of speculation and controversy (see, e.g., the discussion in Ref. [24]). Some evidence exists for a photosubstitution reaction of chlorobenzene in water and water–ethanol mixtures proceeding from the $S_1$ state and a cationic highly reactive intermediate, easily attacked by the solvents [24]. Excitation of the benzene-like chromophore of CLS in the aerated water–acetonitrile mixture leads to both types of reaction with similar efficiencies, as indicated by the formation, with comparable rates, of DCLS and CLS-OH. The observed oxygen effects suggest that while the second reaction proceeds essentially from singlet states, triplet-state contribution to the first reaction path are significant in deaerated samples. Our not finding significant amounts of chlorobenzene among the products indicates that the photoinduced cleavage of the C–S bond, occurring in diphenylsulfone and its diamino derivative [25,26], is not competitive with C–Cl bond cleavage for CLS.

The photochemistry of s-triazine derivatives has been scantily investigated. While halo-diamino-s-triazines in aerated alcohols and water gave substitution of alkoxyl or hydroxyl groups for the halogen, dealkylation of the amino substituents and reductive dehalogenation, methoxy-substituted diamino-s-triazines were unreactive upon irradiation at 254 nm [27,28]. Neither in these nor in a subsequent study on some triamino-s-triazines [29] was the chromophoric ring ever affected by photolysis, as was, instead, the case with asymmetric 1,2,4- [30] and 1,2,3-triazines [31]. This behaviour is confirmed by the substituted-s-triazine chromophore of CLS: irradiation at 254 nm did not result in opening of the triazine ring, as indicated by the absence of the corresponding product containing a polyurea substituent [5,6]. Similarly to the other mentioned s-triazine derivatives, excitation of the triazine chromophore of CLS results in cleavages of some bonds of the sulfonylurea bridge. The products identified result from photodissociation of the S–N, N(1)–C and C–N(2) bonds (paths a, b, c in Scheme 2). These bonds are cleaved following excitation transfer from the triazine chromophore to the sulfonylurea bridge, this transfer being likely driven by a crossing between curves of the lowest excited states of the former and some $\sigma\sigma^*$ dissociative state localised on the bonds of the latter. The primary photoproducts, radicals or ions, may undergo loss of CO and/or react with the solvent to yield the observed compounds. We propose cleavage of the S–N bond (either homolytic or heterolytic) to be a major reaction path when irradiating CLS at 254 nm: CBSAc is, correspondingly, a major benzene-containing product, while the fragment containing triazine likely undergoes thermal loss reactions which compete with formation of TU in the hydrolytic step and yield the other triazine-containing products. CBSA, on the other hand, is a natural result of the N(1)–C bond cleavage in a photoinduced hydrolysis reaction, its triazine counterpart being the triazinyl-carbamic acid TCAc in Scheme 1. Consistently, we observed an almost complete disappearance of the latter product in acetonitrile. Also, in the case of anionic CLS, CBSA is formed with a yield at least three times lower than with neutral CLS and, parallelly, the triazine product is formed in a very low amount. We suggest this to result from an increase in the N(1)–C bond order in the anion with respect to neutral CLS, describable in terms of an increased contribution of the enol limit structure in the valence bond description of the anion. As a consequence, the dissociative curve for this bond will cross the triazine-centred excited states at higher energies than with neutral CLS and the corresponding path will no more be competitive with, e.g., the photocleavage of the S–N bond. Indeed, the anion has a lower photodegradation quantum yield than the neutral form.

As far as triplet-state reactivity is concerned, the much longer lifetime of this state even in air-equilibrated samples probably enables excitation transfer to occur between the two chromophores, therefore leading to a simplified and wavelength-independent reactivity. Although this fact is not fully proved by our experiments, since we could not observe triplet-state properties exciting at wavelengths other than 266 nm, it is suggested by our finding only one $T_1 \rightarrow T_n$ absorption between 300 and 600 nm, characterised by a single-exponential decay kinetics. On the other hand, as a result of strong quenching by oxygen in aerated samples, triplet-state contributions to the photochemistry of CLS are of secondary practical importance in these and, probably, in natural conditions.

## 5. Conclusions

CLS is a diprotic acid that exists as the monoanion in water at pH values between 3.7 and 13.1, i.e., in most natural environments. Its bichromophoric nature is shown by the absorption spectrum, whose features correspond to, essentially, local excitations of the chlorobenzenesulfonyl and of the substituted s-triazine chromophores. As a consequence, CLS acts as the sum of two very weakly interacting photoreactors and exhibits a dependence on the excitation wavelength of both photoproduct distribution and photodegradation quantum yield. While irradiation at wavelengths corresponding to the benzene $L_b$-type band results mainly in reductive dechlorination and substitution of OH for chlorine, light absorption by the triazine chromophore is followed by excitation transfer to the sulfonylurea bridge. The resulting complex product pattern suggests the occurrence of competitive steps involving cleavages of the S–N, N(1)–C and C–N(2) bonds, the first path being the most reactive one. The behaviour in the sunlight reproduces closely that of the benzene chromophore. In deaerated solutions, both singlet and triplet states of the two chromophores contribute to the photoreactivity. The observed triplet state, however, is strongly quenched by oxygen and contributes negligibly to the photoreactions in solutions equilibrated with air. The neutral and anionic forms of CLS exhibit similar photoreactivities, the main differences being due to an increased $\pi$-bond order of the N(1)–C urea bond of the anion. The photodegradation quantum yield was quite low in all cases, from 1 to $5 \times 10^{-2}$ in air-equilibrated solutions. The behaviour in the sunlight reproduces closely that of the benzene chromophore, consistently with the larger overlap of the solar spectrum with the benzene $L_b$-type band than with the hypsochromically shifted triazine-centred bands.

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