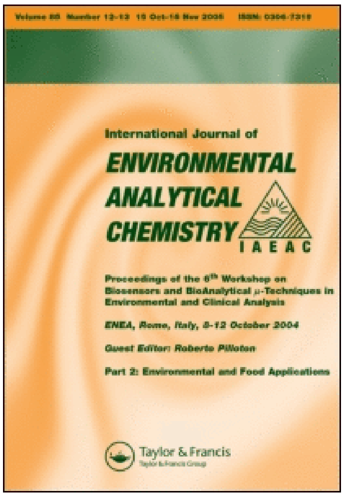

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Investigation of the Photochemistry and Quantum Yields of Triazines Using Polychromatic Irradiation and UV-Spectros Copy as Analytical Tool

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INVESTIGATION OF THE PHOTOCHEMISTRY AND QUANTUM YIELDS OF TRIAZINES USING POLYCHROMATIC IRRADIATION AND UV-SPECTROSCOPY AS ANALYTICAL TOOL

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Photochemical reactions of atrazine, propazine, simazine, terbuthylazine, ametryn and atraton were investigated in aqueous and buffered (pH = 7–9) solutions (containing a few percent of acetonitrile) using a polychromatic Xe light source at T = 22°C. For terbuthylazine the photochemistry is investigated in detail, including solvent-, temperature-and pH-dependence and products found. The role of polychromatic light sources used in investigations of the photochemistry of triazines is discussed.

For the first time, quantum yield measurements were performed in the UV-band between 240–300 nm of the chlorotriazines and ametryn. Isosbestic points were found in the UV-spectra at different irradiation times, and UV-spectroscopy was used to obtain kinetic information.

Quantum yields in aqueous solutions at T = 22°C for the chlorotriazines ($\Phi = 0.048$–0.062) and for ametryn ($\Phi = 0.043$) are comparable. The temperature dependence of the photoreaction of terbuthylazine leads to an activation energy of about 13 kJ mol^{-1}. Quantum yields in acetonitrile and hexane for terbuthylazine are about half of the values found in aqueous solution.

Atraton was not degradable under the conditions used, and the quantum yield could only be estimated to be $\Phi < 0.002$.

KEY WORDS: Triazines, polychromatic irradiation, UV-spectroscopy, HPLC, quantum yields, temperature dependence.

INTRODUCTION

Abiotic degradation of pesticides is mainly attributed to three processes[1–5]: absorption of light (degradation by direct irradiation or sensitized reactions), reaction with radicals (especially OH-radicals) or other highly reactive compounds (photooxidation), and hydrolysis.

As abiotic reactions are (with the exception of hydrolysis) connected with the irradiation by sunlight, most of the degradation reactions take place at day and only a minor portion of the pesticides is degraded at night.

Hydrolysis and biotic reactions are responsible for the degradation in soil and in solution (i.e. in water), a further reaction path is the degradation by light. Photooxidative processes and light-induced reactions are responsible for the degradation of pesticides in air. However, although the principle reaction paths for the degradation of pesticides in the environment are known, detailed measurements of individual reactions and

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* Corresponding author.

experimentally determined half-lives are rare, and estimation methods such as QSAR[6] are often used to predict loss paths relevant to the environment.

The present paper deals with photochemical reactions (especially the measurement of quantum yields) of triazines, widely used as herbicides.

The triazine family is one of the best-investigated classes of pesticides with respect to photochemical reactions. First, detailed investigations about the photochemistry of triazines were performed by Pape and Zabik[7,8]. Especially numerous product studies for 2-chlorotriazines were performed, and the corresponding hydroxytriazines are identified as main products in direct photolysis[7,9,10] besides some minor products[11].

In contrast to direct irradiation the chloro substituent is retained in oxidation reactions (often performed by photolysis of ozone or hydrogen peroxide and initiated by OH-radicals). Main products found are desalkyl triazines and ketones (by reaction at the side chain of the triazines[12–14]), recently also found in the gas-phase[15]. Hence, the product distribution appears to be a useful tool to distinguish between the different reaction paths involved.

A change at least in product distribution was found in photochemical reactions using additives like iron salts[17], photo-sensitizers such as acetone[16] or methylene blue[18] and in the presence of TiO_2[19–22].

Nevertheless, besides reported quantum yields of some chlorotriazines, especially of atrazine[10,23,24] and the corresponding desalkyl derivatives[10], determined at $\lambda = 254$ nm, photo-physical properties, quantum yields and their dependencies on solvent, pH or temperature of triazines are almost unknown. Moreover, large variations of photolytic rate constants of triazines were found using artificial sun-like lamps (often poorly characterized).

The present paper discusses the UV-spectra of atrazine, propazine, simazine, terbuthylazine, ametryn and atraton and the importance of the light source used in the investigation of the photochemistry of triazines (see Table 1).

A simple approach to investigate photochemical reactions and quantum yields in solution (so far never used before for triazines) is to use the spectral and kinetic information of the corresponding UV-spectra. Quantum yields were determined for the first time after excitation in the UV-band between 240–300 nm using a polychromatic Xe light source. Most of the measurements were performed for terbuthylazine in continuation of recently performed investigations of photooxidative reactions in the gas phase[15].

EXPERIMENTAL SETUP AND EVALUATION OF RAW DATA

Instrumentation

UV-spectra (double beam spectrometer Uvikon 860, Kontron Instruments) were measured at d = 1 cm in quartz cuvettes with the corresponding solvent as reference. The wavelength accuracy has been checked to be better than $\Delta\lambda = \pm 1$ nm. The lowest measurable absorbance can be estimated to be $E \approx 0.004$. For the calculation of the molar absorption coefficients various concentrations were used to obtain absorbances in the region 0.05–1.8. Spectra were measured at ambient temperature ($T \approx 298$ K). Temperature dependencies were examined using thermostated cuvette holders in the UV-spectrometer.

A modified merry-go-round apparatus (DEMA, Bornheim; Germany) with simultaneous irradiation of 10 cuvettes (optical pathlength 1 cm) has been used for all irradiation experiments with a Xe lamp XOP7 (500 W, Philips; Germany) as the light source. The distance of the light source from the cuvettes is about 5 cm, the irradiated volume was always 3.5 ml. Cooling is accomplished by three cooling circuits: the Xenon lamp by pressurized air ($T_{in} \approx 293$ K, $T_{out} \approx 383$ K) and tap water, the temperature bath with the cuvettes by a thermostat. The temperature in the cuvettes (usually T = 295 ± 2 K) was determined after an equilibration period using a standard laboratory thermometer. Higher temperatures in the cuvettes were obtained by changing the temperature of the thermostat only. Different cut-off wavelengths were achieved using double walled cooling jackets for the Xenon lamp made of Duran—or quartz-glass and additional optical filters with selected thickness made of Duran-glass.

For atraton, measurements were performed also with a low pressure mercury lamp (Penray with an UG11-optical filter (Schott)) with most of the intensity at $\lambda = 254$ nm.

HPLC-analysis was performed with a Waters QA-1 autosampler system (UV-detection at 254 nm, column: C18-4 µm, flow: 1.5 ml/min, AUFS: 0.1, solvent: 60/40% acetonitrile/water).

All solvents used had HPLC quality (Aldrich). Propazine (98.1%), ametryn (98.4%) and atraton (98.6%) were used as received from Ehrenstorfer (Germany), atrazine (98%), simazine (99%) and terbuthylazine (99%) were used as received from Riedel de Haën (Germany). Hydroxyterbuthylazine, desethyl—and des-tert-butylterbuthylazine were received (> 98%) from Ciba-Geigy (Switzerland).

Commercial buffer solutions (Merck) were used for pH = 6, 7 and 9. Standard solutions of hydrogen chloride were used to obtain pH-values below 6. Atrazine was dissolved in water and diluted with buffer solution (pH = 9). Different concentrations for all other compounds were obtained from stock solutions in acetonitrile by dilution with water or a water/buffer mixture. The concentrations and mixtures used are given below.

For irradiation experiments, 3.5 ml of the corresponding solution were filled into a quartz cuvette, stoppered by a teflon stopper and placed into the merry-go-round apparatus. The time required to place the cuvette into the irradiation apparatus (some seconds) is negligible compared to the irradiation time (hours). At desired irradiation times, the cuvette was removed, a UV-spectrum recorded, and the same cuvette replaced into the apparatus. Cuvettes were never opened during the measurement. For terbuthylazine, the analysis by UV-spectroscopy was examined in two experiments by HPLC. In these cases, one cuvette per irradiation time was used, and the solution was analyzed besides UV-spectroscopy by HPLC.

Calculation of rate constants

Rate constants k_i were obtained from a non-linear fit of the absorbances $E_{\lambda,t}$ of the corresponding compound versus the irradiation time t for all wavelengths according equation (1).

$$E_{\lambda,t} = (E_{\lambda,0} - E_{\lambda,\infty}) \cdot exp\,(-k_i \cdot t) + E_{\lambda,\infty} \tag{1}$$

with $E_{\lambda,0}$ taken from the UV-spectrum at t = 0 and $E_{\lambda,\infty}$ obtained as second fit parameter. As absorbances were not determined at equidistant time intervals we did not use the method according to Guggenheim. A detailed discussion of the method used is given elsewhere[27].

With the exception of atraton, a mean rate constant k (with no weighting) was calculated from the rate constants k_i obtained in the wavelength region $\lambda = 200$–280 nm but excluding the wavelengths (about ± 3 nm) around the isosbestic points (see discussion). Concentrations c(t)/M at the corresponding irradiation times were calculated from c(t) = c(0) · exp(−k · t) using the concentration c(0)/M at time t = 0 (start of the irradiation).

Actinometry and calculation of quantum yields

For the measurement of the relative light intensities $J_{rel,\lambda}$ of the xenon lamp XOP7 (with the corresponding cooling jacket and, if necessary additional optical filter), a monochromator M300 HRA (Bentham) and a photomultiplier 1P28 (RCA) was used. The spectral resolution was about 2 nm, and spectra were measured in 1 nm steps. To correct for the spectral transmission of the monochromator and for the response of the photomultiplier, a quartz halogen lamp standard was used (Model 63361, Oriel).

Absolute light intensities $J_{abs,\lambda}$ were determined using the ferrioxalate actinometer[25] (reduction of Fe (III) to Fe (II)). The decrease of quantum yield of the ferrioxalate for high wavelengths was considered using equation (2)

$$F_{abs} = \frac{N_A \cdot \Delta n_A}{V \cdot \Delta t \cdot \Sigma_{\lambda_2}^{\lambda_2} \{\Phi_{A,\lambda} \cdot J_{rel,\lambda} \cdot (1 - 10^{-E_{A,\lambda}})\}} \qquad (2)$$

The quantum yield of the production of Fe(II) ($\Phi_{A,\lambda}$) as a function of wavelength in 1 nm-steps is obtained from a polynominal fit using values from the literature[26], $J_{rel,\lambda}$ is the relative light intensity, $E_{A,\lambda}$ is the absorbance of the actinometer, Δn_A/mole the moles Fe (II) produced (measured by UV-spectroscopy as phenanthroline complex), V/cm^3 the irradiation volume, t/s the irradiation time and N_A Avogadro's number.

$J_{abs,\lambda}$/photons s^{-1} nm^{-1} cm^{-3} = F_{abs}/photons s^{-1} cm^{-3}. $J_{rel,\lambda}$/nm^{-1} is the available wavelength dependent, absolute light intensity of the light source under the conditions used. The light intensity $J'_{abs,\lambda}$ absorbed by the compound under consideration was calculated using equation (3).

$$J'_{abs,\lambda} = J_{abs,\lambda} \cdot \left(\frac{1 - 10^{-E_\lambda}}{E_\lambda}\right) \cdot \varepsilon_\lambda \cdot c(t) \qquad (3)$$

with the absorbance E_λ determined by UV-spectroscopy and the corresponding molar absorption coefficients ε_λ/M^{-1} cm^{-1}.

The quantum yield Φ was calculated from a plot of the left hand side of equation (4) versus irradiation time.

$$\frac{[c\,(0) - c\,(t)] \cdot N_A}{1000 \cdot \Sigma_{\lambda_1}^{\lambda_2} J'_{abs,\lambda}} = \bar{\Phi} \cdot t \qquad (4)$$

RESULTS AND DISCUSSION

Static UV-spectra of triazines

Molar absorption coefficients, especially for chlorotriazines at the maxima of the UV-bands, were reported before in the literature[9,10,28-30].

However, exact UV-spectra of the chlorotriazines are still poorly known, especially in the wavelength region above 280 nm relevant for the degradation by direct irradiation in the environment. As an example, atrazine should absorb light only below 280 nm[31] in contradiction to a reported weak absorption in the region 300–350 nm[11].

The UV-spectra of the triazines investigated in this study are shown in Figure 1. For comparison and to increase the solubilities all spectra were determined in water with additional 5% of acetonitrile.

The UV-spectra of atrazine, simazine and propazine are within the error of the measurement comparable, whereas small deviations were found for terbuthylazine with respect to the other chlorotriazines. All chlorotriazines show two distinct absorption bands with $\lambda_{max} \approx 225$ nm and 265 nm. After substitution of chloro by thiomethyl in the case of ametryn a third UV-band at about 245 nm was observed as a shoulder increasing the molar absorption coefficients in the region 230–280 nm. On the other hand, the substitution of chloro by methoxy in the case of atraton decreases the molar absorption coefficients in the region 250–300 nm with respect to the other triazines and the band at higher wavelengths is observed only as weak shoulder.

Detailed measurements of the UV-spectrum of terbuthylazine lead to molar absorption coefficients $\varepsilon_{300} = 3.2$ M^{-1} cm^{-1} and $\varepsilon_{>310} < 1$ M^{-1} cm^{-1} in filtered (0.45 μm) methanol solutions using high concentrations (0.005 M). We indeed assume, that for the chlorotriazines in general no further UV-band exists above 310 nm, and impurities are

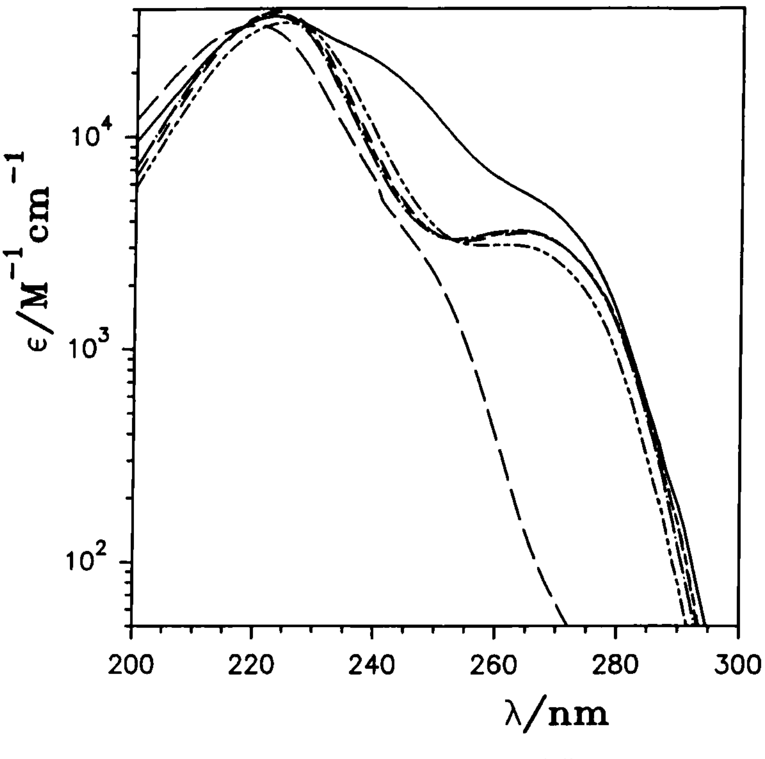


Figure 1 UV-spectra of the triazines investigated in water/5% acetonitrile (—— ametryn, — — atraton, - - - - atrazine, - · - · propazine, – – – simazine, — - - — terbuthylazine).

most probably responsible for tails observed in the UV-spectra. Further measurements with ultrapure compounds may confirm this assumption.

The solvent dependence of the UV-spectrum of terbuthylazine is shown in Figure 2. For both UV-bands, a bathochromic shift of about 5 nm was found with increasing polarity of the solvent (hexane → acetonitrile → water/5% acetonitrile). Both bands are therefore assigned to $\pi - \pi^*$ transitions, confirmed by the high molar absorption coefficients which excludes $n - \pi^*$-transitions[32]. For atrazine, a comparable bathochromic shift in the UV-spectrum with increasing polarity of the solvent was reported[7] for the UV-band at 222 nm.

UV-spectra of the chlorotriazines are comparable at pH 4–9, respectively. At pH values below the pK_S (pH < 2) strong bathochromic shifts were found as reported before in the literature[28]. However, no experiments were performed in the present study for pH < 2.

Discussion of the importance of the light source used in photolysis experiments of triazines

The spectral distributions of the XOP7-Xe light source used to investigate the photochemistry of triazines are shown in Figure 3. For the determination of rate

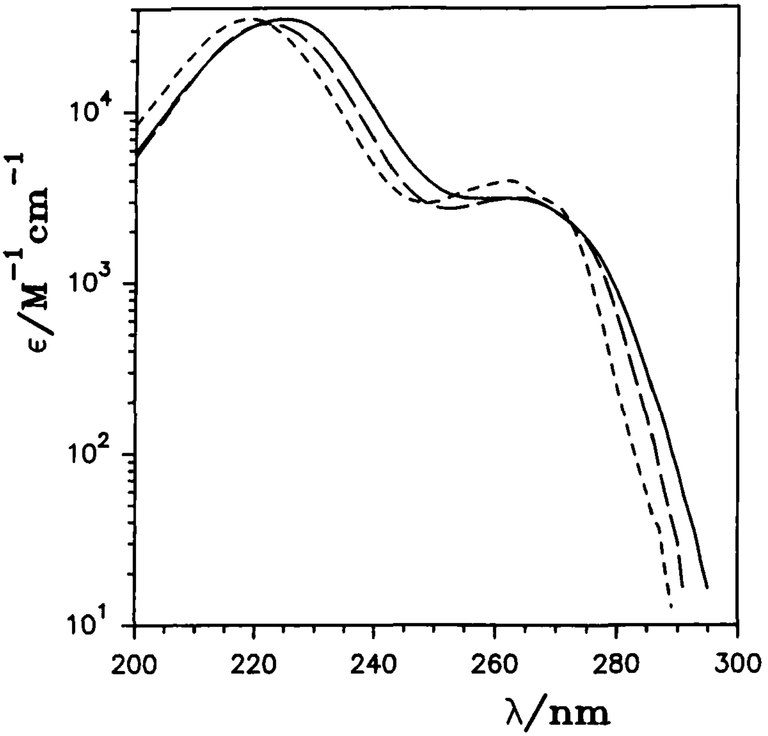


Figure 2 Solvent dependence of the UV-spectra of terbuthylazine (—— water/5% acetonitrile, – – – acetonitrile, - - - - hexane). From the bathochromic shift with increasing solvent polarity both bands are assigned to $\pi - \pi^*$ transitions.

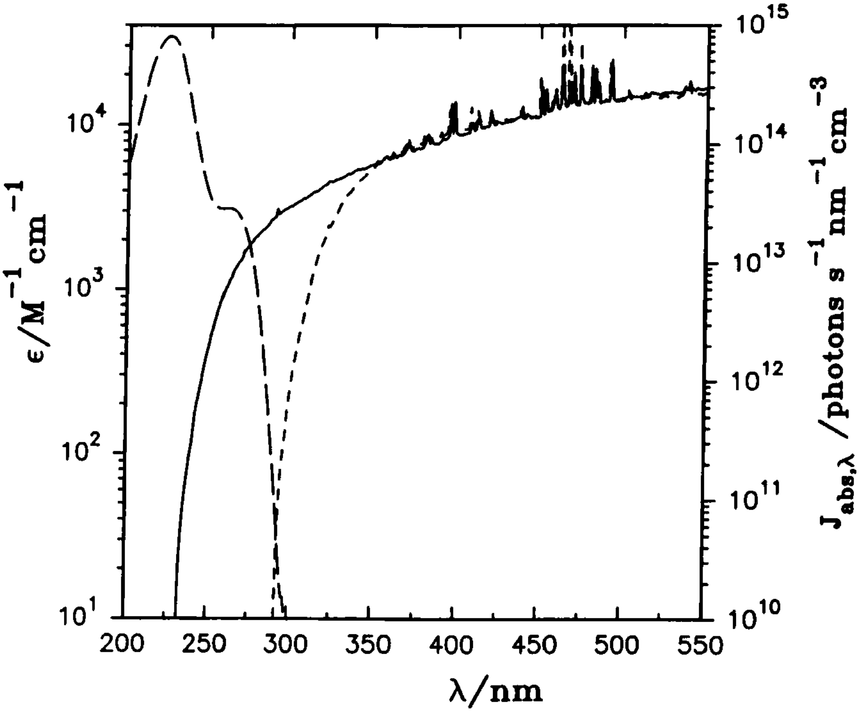


Figure 3 Absolute wavelength dependent light intensities of the Xe light source used with a quartz cooling jacket (——) and a Duran cooling jacket + additional optical filter (– – – , sun-like light source) calculated from actinometric measurements and relative intensities. For comparison of the overlap the UV-spectrum of terbuthylazine (— — —) in water/5% acetonitrile is included.

constants and quantum yields the quartz cooling jacket was used without exception. For comparison and to demonstrate the overlap of the light intensities of the light source and the UV-spectra of the triazines the UV-spectrum of terbuthylazine as a typical member of the chlorotriazines is included in Figure 3. For investigations of photochemical reactions with a light source comparable to sunlight we used a Duran glass cooling jacket with an additional optical filter. The corresponding light intensities are also included in Figure 3 (dashed line).

The absolute intensities presented in Figure 3 were calculated from actinometric measurements. The absolute intensity of the Xe light source with the quartz cooling jacket in the wavelength region 240–550 nm was ($J_{abs} \pm 2\sigma$) = (5.0 ± 0.5) $\cdot$ 10^{16} photons s^{-1} cm^{-3}. The light intensities were stable within the total irradiation time for all experiments performed in this study (about 100 hours).

The absolute light intensities using the quartz cooling jacket or the Duran cooling jacket in the wavelength region 240–550 nm are, within the error of the actinometric measurements, comparable. However, for the relevant wavelength region between 240–300 nm the absolute intensities are completely different. Information only about the integrated absolute intensities for polychromatic irradiations is therefore not useful.

Only a very small overlap of the sun-like light source (Xe lamp with Duran jacket) with the UV-spectra of the chlorotriazines and ametryn is obtained whereas no overlap exists for atraton. Therefore, this light source is not useful to investigate the photochemistry of these compounds. However, guidelines[33] recommend to use light sources with $\lambda > 290$ nm in measurements of quantum yields if the molar absorption coefficient at $\lambda = 295$ nm is higher or equal to $\varepsilon = 10\ M^{-1}\ cm^{-1}$ which is fulfilled in the case of some of the triazines. Moreover, UV-spectra of other pesticides such as urea-derivatives[34] are comparable to triazines in the region around 300 nm with respect to their molar absorption coefficients. For exact quantum yield measurements of these compounds and especially for triazines we therefore strongly recommend to use a light source with measurable intensities below 290 nm as performed in this study. However, to our knowledge quantitative measurements were only performed at $\lambda = 254$ nm (mercury light sources), and we present for the first time quantum yield measurements after excitation in the UV-band between 240 nm and 300 nm.

UV-spectra of irradiated solutions

The time dependent UV-spectra of propazine and ametryn in water/5% acetonitrile as typical examples are shown in Figures 4 and 5. For both compounds isosbestic points were found (for propazine at $\lambda_{iso} = 209.5$, 233.5 and 255.0 nm, for ametryn at $\lambda_{iso} = 208.5$ nm).

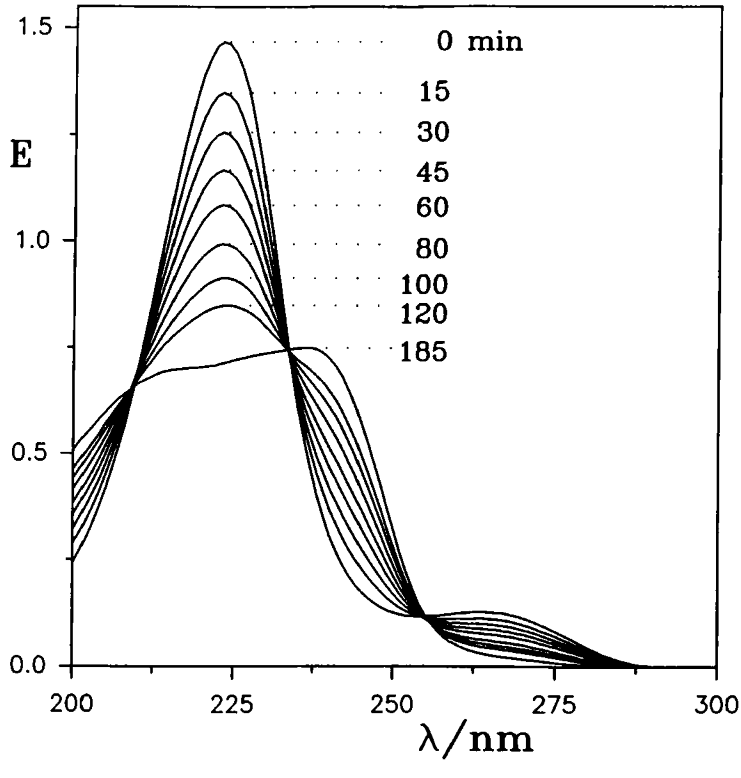


Figure 4 UV-spectra of propazine in water/5% acetonitrile (c(0) = 3.81 · 10^{-5} M) for different irradiation times.

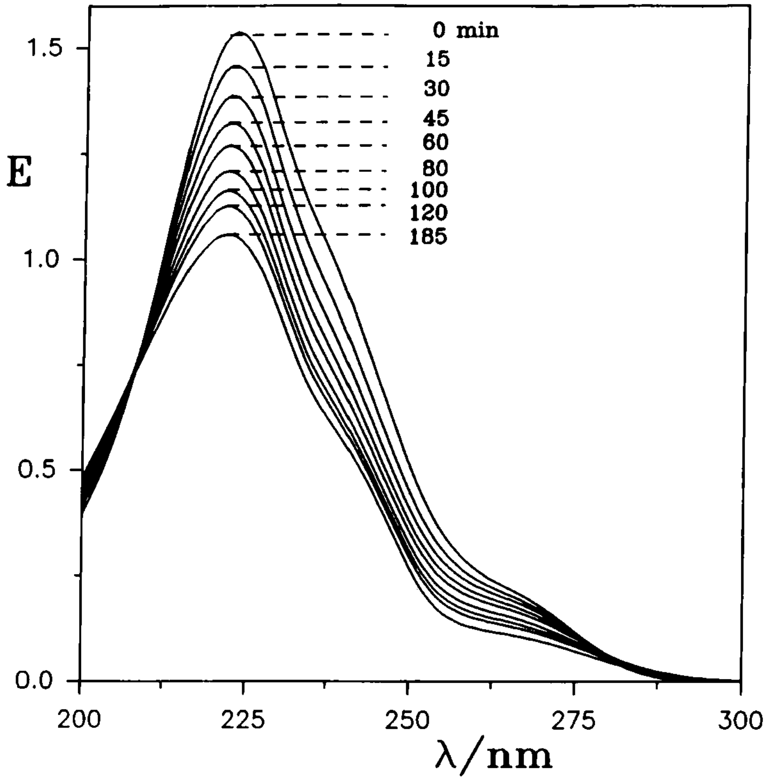


Figure 5 UV-spectra of ametryn in water/5% acetonitrile ($c(0) = 4.19 \cdot 10^{-5}$ M) for different irradiation times.

The triazines react in a uniform photochemical reaction. This can be shown using the differences of absorbances (also called *Mauser*-diagrams—a detailed discussion can be found elsewhere[27]). Propazine may serve here as an example. Using the data from Figure 4 a plot of the differences of the absorbances at 5 different wavelengths which cover the wavelength region from 205–260 nm versus the absorbance differences at $\lambda = 224$ nm as reference wavelength is shown in Figure 6. Straight lines were found for all wavelengths, indicating a uniform reaction. Ametryn and chlorotriazines react therefore in a uniform reaction $A \rightarrow B + C + ...$

However, for very high conversions (> 80%) small deviations in the isosbestic points were found, probably as a result from a photoreaction of by-products from photolysis of the triazines.

Nevertheless, a single, major product was found in all cases as confirmed by HPLC. As well known in the literature for chlorotriazines this product is the corresponding hydroxytriazine[7–11,16] and for ametryn the 2-H derivative 4-ethylamino-6-isopropylamino-s-triazine[7]. Product studies for direct photolysis of atraton have not been published before to our knowledge.

Although detailed product studies were not performed we identified hydroxyterbuthylazine as the main product in the case of terbuthylazine (confirmed by comparison with an authentic sample) in a yield of 90–95% (in water/5% acetonitrile)

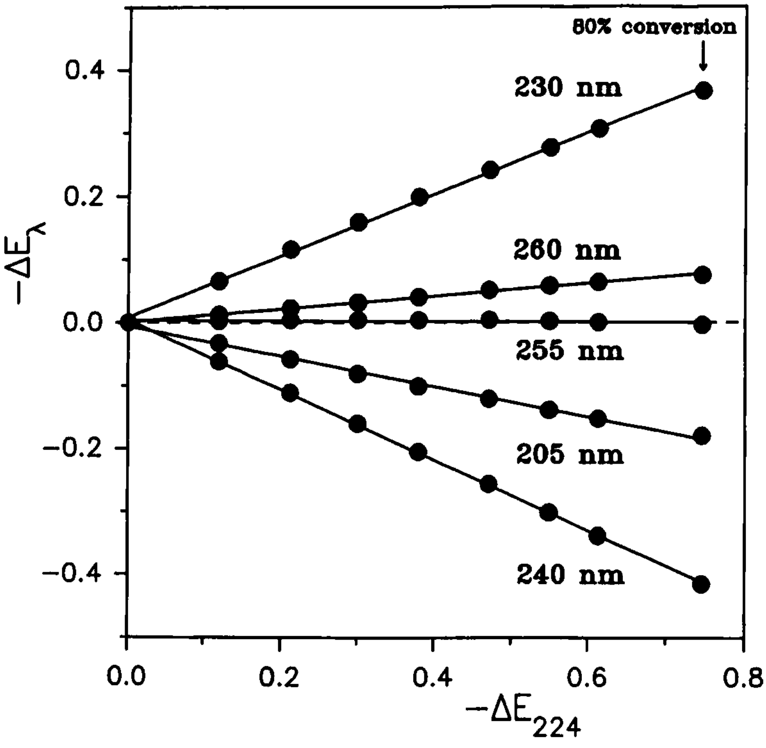


Figure 6 Differences of absorbances for propazine at five wavelengths versus the absorbance difference at 224 nm using the data shown in Figure 4. For clarity data for one of the isosbestic points are included only (λ = 255 nm). The dashed line indicates no change of absorbance with irradiation time.

whereas desethyl-and des-tert-butylterbuthylazine were never found in irradiated solutions. As in aqueous solutions, different major products were found in acetonitrile and in hexane in photolysis experiments with atrazine and terbuthylazine with up to now unknown structures.

The time dependent UV-spectra are dominated by the corresponding hydroxytriazines as main products in the photolysis of the chlorotriazines. We therefore were highly surprised, when no isosbestic points were found in water/5% acetonitrile in first experiments with atrazine and simazine. On the other hand (as shown in Figure 7 for terbuthylazine), different isosbestic points were found in water/5% acetonitrile (λ_{iso} = 209.5, 234.5 and 257.0 nm) and in buffer pH = 9/4% acetonitrile (λ_{iso} = 211.5, 235.0 and 252.5 nm). However, independently determined UV-spectra of hydroxyterbuthylazine (see Figure 7) in buffer pH = 9/5% methanol and at pH = 2.7/5% methanol show a strong dependence on pH-value as known for other hydroxytriazines[28,35]. The analysis[35,36] at λ = 253 nm from the UV-spectra of hydroxyterbuthylazine at pH = 9, 7, 6, 4 and 2.7 (with 5% methanol, respectively) leads to a $pK_A \approx 4.9$, in accordance with $pK_A = 5.2$ for hydroxypropazine[35]. As can be seen from Figure 7 the UV-spectrum of pure hydroxyterbuthylazine confirms the isosbestic points found in the photolysis at pH = 9, and we assume a fairly quantitative conversion of terbuthylazine to hydroxyterbuthylazine. On the other hand, deviations were found in the corresponding

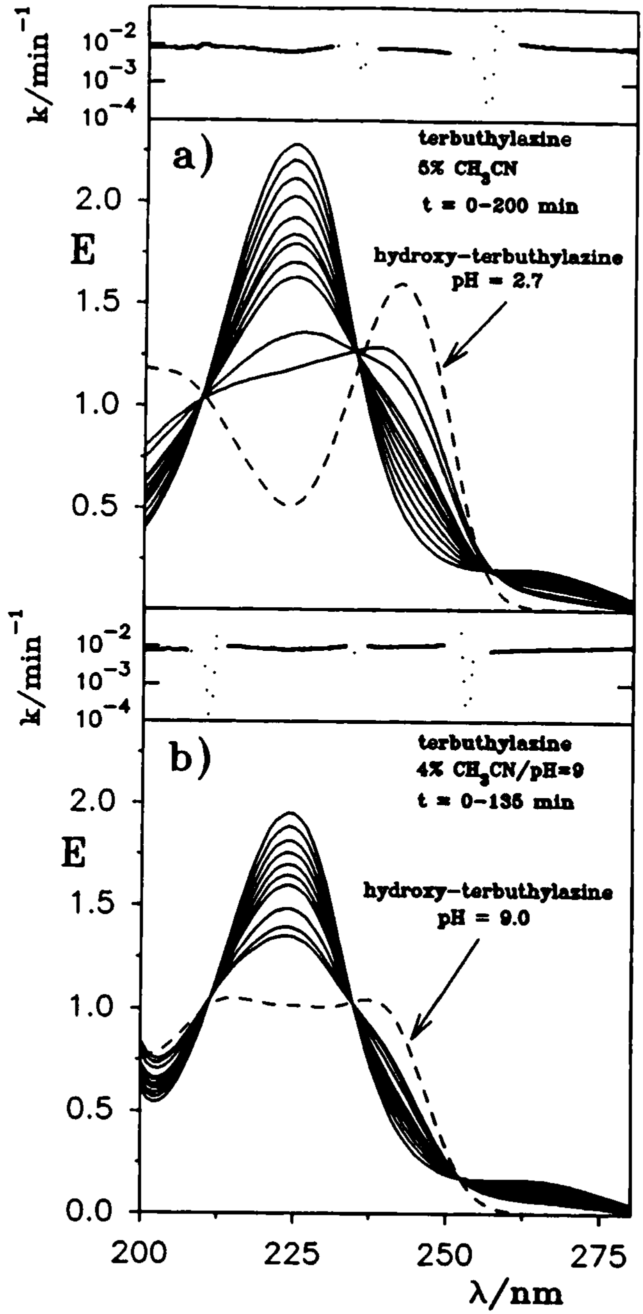


Figure 7 UV-spectra at different irradiation times and calculated rate constants (k/min^{-1}) using the absorbance at the corresponding wavelengths for terbuthylazine (——) in a) water/5% acetonitrile, c(0) = 6.69 · 10^{-5} M and b) buffer pH = 9/4% acetonitrile, c(0) = 5.36 · 10^{-5} M.

Also shown are the UV-spectra of hydroxyterbuthylazine (- - - -) at a) pH = 2.7/5% methanol and at b) pH = 9/5% methanol. The absorbances determined for c(0) = 4.23 · 10^{-5} M were rescaled to the concentrations of the corresponding terbuthylazine solutions, respectively.

photolysis in unbuffered aqueous solution in accordance with a 5–10% conversion of terbuthylazine to minor by-products.

Isosbestic points were not found for atrazine and simazine in unbuffered aqueous solutions due to a change of pH with a corresponding change of the UV-spectrum of the hydroxytriazines. Hence, isosbestic points were found again in irradiation experiments with atrazine (λ_{iso} = 211.0, 233.0 and 250.5 nm) and simazine (λ_{iso} = 211.5, 232.5 and 250.0 nm) in buffered solutions at pH = 9.

Nevertheless, isosbestic points found in the case of terbuthylazine and propazine in aqueous solutions are in direct contrast to the results found for atrazine and simazine and a more detailed investigation about the pH-dependence of the UV-spectra of the corresponding hydroxytriazines should clarify this discrepancy.

Photolytic rate constants and quantum yields

To employ monoexponential kinetic schemes in photochemical reactions, absorbances at the excitations wavelengths must be well below 0.2[36]. A main aim of the study was to calculate rate constants using the information from the UV-spectra in the wavelength region 200–280 nm. Therefore, absorbances should be relatively high, and the concentrations for all solutions were chosen to give an absorbance at the start of the experiments of about 0.2 at 265 nm. As absorbances above 265 nm decrease but intensities of the light source strongly increase for higher wavelengths, the calculation of rate constants is admissible. This is checked by two independent irradiation experiments of terbuthylazine in water/5% acetonitrile, which were analyzed by HPLC and by comparing with the corresponding rate constants calculated for all wavelengths from the UV-spectra shown in Figure 7. The concentrations obtained by HPLC are displayed in Figure 8 and are in accordance with the mean rate constant calculated from the corresponding UV-spectra. In general, rate constants were found to be identical within the error of the experiment in the wavelength region 200–280 nm, as shown for terbuthylazine as an example at two different pH-values in Figure 7. Again, this confirms a uniform reaction of the triazines investigated (with the exception of atraton) as shown before for propazine using the differences of absorbances (Figure 6). Rate constants determined close to the isosbestic points (about ± 3 nm) were not used in the calculation of the mean rate constant. All rate constants and the corresponding quantum yields determined are summarized in Table 2. With the exception of atraton, all compounds investigated were degradable using the Xe lamp with quartz jacket, and half-lives of about 1–2 hours were obtained. No conversion (within an error of 3%) was found for atraton after 4 hours irradiation either using the Xe lamp nor using the mercury light source (λ = 254 nm, absolute intensity was determined to be $J_{abs} = 3.0 \cdot 10^{14}$ photons s^{-1} cm^{-3}).

Using the Xe lamp with Duran jacket (sun-like light source) no conversion was found for terbuthylazine (within an error of 3%) after 24 hours irradiation.

Irradiation times and corresponding half-lives reported in the literature for irradiation of chlorotriazines in solution (in particular for atrazine) at λ_{ex} = 254 nm are low in the region of minutes to some hours[7,10,24,37]. On the other hand, strong differences were reported for the disappearance rate constants of atrazine as the most prominent member of the chlorotriazines for wavelengths $\lambda \geq 290$ nm. For stated wavelengths $\lambda \geq 290$ nm of artificial polychromatic light sources half-lives of 1.5h[38] and 25 hours[16,17], for $\lambda \geq 340$ nm a half-life of about 1 month was reported[11]. For sunlight (assuming $\lambda \geq 290$ nm) half-lives of 390 hours[17] to more than 3 months were found[39]. More and comparable values can be found also in a recently published compilation[11].

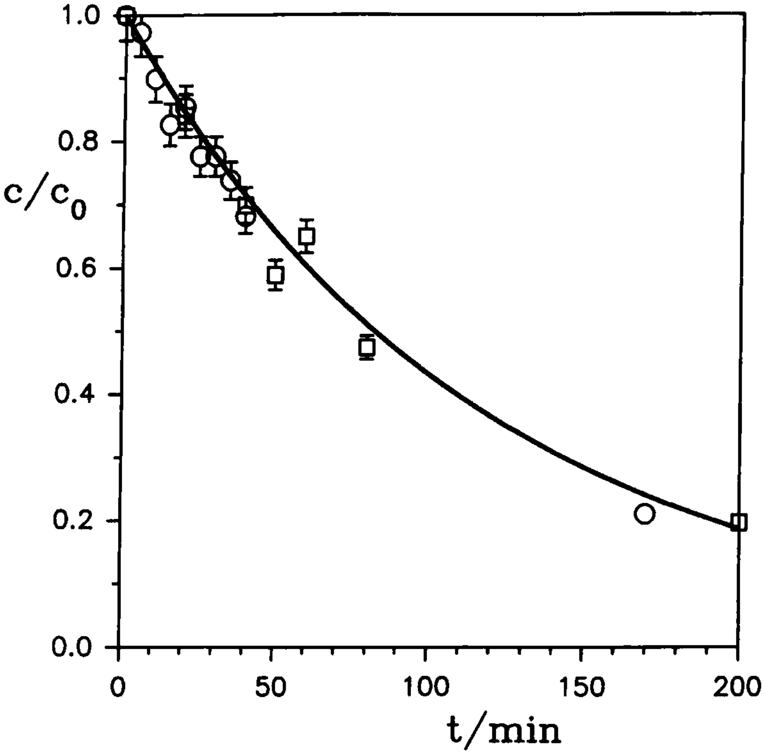
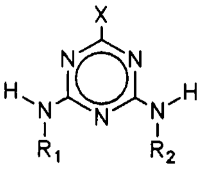


Figure 8 Normalized concentrations of two independent irradiations of terbuthylazine in water/5% acetonitrile (c(0) = 6.69 · 10^{-5} M) analyzed by HPLC (○, □) and for comparison the exponential loss (——), (k ± 2σ) = (0.0088 ± 0.0005) min^{-1}, as calculated from the corresponding UV-spectra.

Table 1 Substitution patterns of the triazines investigated, and derivatives of terbuthylazine.



s-triazine	*X*	*R_1*	*R_2*
atrazine	Cl	CH_2CH_3	$CH(CH_3)_2$
propazine	Cl	$CH(CH_3)_2$	$CH(CH_3)_2$
simazine	Cl	CH_2CH_3	CH_2CH_3
terbuthylazine	Cl	CH_2CH_3	$C(CH_3)_3$
hydroxy-" -	OH	CH_2CH_3	$C(CH_3)_3$
desethyl-" -	Cl	H	$C(CH_3)_3$
des-tert-butyl-" -	Cl	CH_2CH_3	H
ametryn	SCH_3	CH_2CH_3	$CH(CH_3)_2$
atraton	OCH_3	CH_2CH_3	$CH(CH_3)_2$

Table 2 Rate constants (k) and quantum yields (Φ) determined in different solvents. Measurements were performed with the Xe light source with quartz cooling jacket as shown in Figure 3.

Solvent	*$c_0/10^{-5}$ M*	*T/°C*	*k/min^{-1} (a)*	*Φ (b)*	*Comment*
		Atrazine			
Water	≈ 0.8	—	—	0.050	254 nm[10]
Water	≤ 0.1	20	—	0.051	254 nm[23]
Water	0.38	—	4.3	0.038	254 nm[24]
Buffer pH = 9	5.98	22	0.01	0.061	this work
Acetonitrile	3.95	22	0.0043	0.026	this work
		Propazine			
Water	≈ 0.8	—	—	0.099	254 nm[10]
Water/5% CH_3CN	3.81	22	0.0084	0.048	this work
		Simazine			
Water	≈ 0.8	—	—	0.083	254 nm[10]
Buffer pH= 9/5% CH_3CN	5.49	22	0.010	0.060	this work
		Terbuthylazine			
Water	≈ 0.8	—	—	0.094	254 nm[10]
Water/5% CH_3CN	6.70	22	0.0088	0.060	this work (c)
Buffer pH= 9/4% CH_3CN	5.36	22	0.0094	0.062	this work
Buffer pH= 7/1% CH_3CN	5.12	20	0.0092	0.062	this work
Buffer pH= 7/1% CH_3CN	4.98	35	0.0126	0.083	this work
Buffer pH= 7/1% CH_3CN	5.12	51	0.0153	0.105	this work
Acetonitrile	4.62	22	0.0044	0.033	this work
Hexane	5.49	22	0.0033	0.027	this work
		Ametryn			
Water/5% CH_3CN	4.19	22	0.013	0.043	this work (c)
		Atraton			
Water	9.35	22	—	< 0.002	this work (d)

(a) Statistical errors: 2σ = ± 5%. (b) Statistical errors: 2σ = ± 10%. (c) The same quantum yield was found in solutions saturated with oxygen or nitrogen. (d) Atraton was not degradable under the conditions used and the quantum yield given is the maximum value calculated from the uncertainties (3%) of the analytical equipment. Approximately the same limit for Φ was found using a low pressure mercury lamp at λ = 254 nm.

Only a few investigations exist about rate constants for the direct irradiation of ametryn[7,17,37] and atraton[37].

The strong differences of half-lives of chlorotriazines for stated irradiation wavelengths above λ = 290 nm are understandable. Since the overlap of (the solvent dependent) UV-spectrum and the light intensity of the artificial sun-like light sources in the region around 290 nm is extremely low, small differences in the spectral distribution of the polychromatic light sources are expected to have dramatic effects on the rate constants found. The same holds for the natural sunlight between 290–310 nm with a strong change of the light intensity depending on latitude and season and certainly on time of the day[40]. Another aspect of the photochemistry of triazines is the temperature dependence. Up to now the influence of temperature on the photochemistry of triazines was not considered. Temperatures ranging from 20–25°C[7,31,37,41], 35°C[17], 40–44°C[9,18,38,42] to 60°C[11] were reported in photochemical investigations of chlorotriazines. We examined the temperature dependence of the photochemical degradation of terbuthylazine in buffer pH = 7/1% acetonitrile in the range 20–51°C and found an increase of the rate constant of about 60% (see Table 2). No change in the UV-spectrum of terbuthylazine in a temperature range of 10–60°C was found and we calculate an increase of the quantum yield from 0.062 to 0.105. The Arrhenius plot leads to an activation energy of $E_A = 13$ kJ mol^{-1}.

Although statistical errors of the quantum yields given in Table 2 are only about 10%, an overall error of 20% has to be admitted to include the uncertainty of the spectral overlap and variations of the lamp intensity. Considering a comparable temperature dependence for other chlorotriazines and errors of about 20% the quantum yield of atrazine at 22°C found in this study ($\Phi = 0.061$) is in good agreement with previous values (see Table 2). The quantum yields of simazine, propazine and terbuthylazine determined in this study at room temperature are comparable to atrazine and are about 50% lower with respect to the values determined in a study with excitation wavelength 254 nm[10]. The quantum yield of atrazine and terbuthylazine in acetonitrile and for terbuthylazine in hexane are about half of the values determined in aqueous solution.

Although the rate constant for photolytic degradation of ametryn is higher with respect to the chlorotriazines, the quantum yield ($\Phi = 0.043$) is about 20% lower due to higher molar absorption coefficients.

Atraton was not degradable under the conditions used, and the quantum yield ($\Phi < 0.002$) was estimated using the error of the analytical equipment. However, the quantum yield of atraton is at least a factor 40–60 lower than the corresponding quantum yields of the chlorotriazines and ametryn. The related hydroxytriazines are known to be photostable[10], and similar low quantum yields are assumed for these compounds confirmed by isosbestic points found in the photoreaction of the chlorotriazines.

No difference in quantum yields at 22°C was found for terbuthylazine and ametryn for solutions deoxygenated by nitrogen or treated with oxygen.

Only a few data exist about photophysical properties of triazines, and mechanistic details about the photochemistry are still missing. Fluorescence- and phosphorescence spectra of the triazines investigated in this study are not known. Hence, whether the singlet state or after intersystem crossing the triplet state is responsible for the photoreaction of triazines is unknown. However, the reacting state is only slightly influenced by oxygen as known for atrazine[10] and confirmed for terbuthylazine and ametryn in this study, which excludes a long-lived triplet state. The sensitising reaction assumed in the system acetone/atrazine[8,16] is rather uncertain and to our opinion doubtful. The triplet state of acetone (E_T = 330–340 kJ mol^{-1})[32] is lower in energy than the corresponding triplet state of the unsubstituted s-triazine ($E_T \approx 360$ kJ mol^{-1} in the vapour state[43]). Furthermore, UV-bands between 240–300 nm of chlorotriazines show a hypsochromic shift with respect to the unsubstituted s-triazine[44]. Assuming a shift of the triplet state comparable to the shift of the singlet state a sensitation reaction of chlorotriazines by acetone is highly improbable.

The participation of ionic intermediates is discussed in the photoreaction of chlorotriazines[8,10]. This assumption is based especially on related reactions of haloaromatics and on the products found. Hydroxytriazines are produced in aqueous solutions, whereas ethers are formed in the corresponding alcoholic solutions[8]. On the other hand, we propose a pure radical reaction in the case of ametryn due to the formation of the 2-H derivative in unpolar as well as in polar solvents[7]. Nevertheless, the quantum yields of both reactions are comparable in aqueous solutions.

Atraton is practically photo-stable[7] as deduced in this study from the UV-spectrum and the very low quantum yield. In contrast to a reported[16] relatively short half-life of about 82 h using artificial sunlight our measurements exclude a degradation of atratone using light sources with intensities above 290 nm.

CONCLUSIONS

Analysis of UV-spectra of triazines leads to a fast and precise method to obtain photochemical rate constants and quantum yields, and some examples were presented to show the capabilities of the method.

The photolysis of terbuthylazine was investigated in detail. No difference in quantum yields ($\Phi = 0.060$–0.062) was found for terbuthylazine in unbuffered aqueous solutions and at pH = 7 and pH = 9, whereas a slight decrease of the photolytic degradation with increasing pH was reported for atrazine[37]. Quantum yields obtained in acetonitrile and hexane are lower by a factor of 2. The photolysis of terbuthylazine shows a slight temperature dependence with an Arrhenius activation energy of about 13 kJ mol^{-1}.

Considering the dependencies found in the photolysis of terbuthylazine and errors of about 20%, the quantum yields obtained for all chlorotriazines are comparable with the few values known in the literature. Since all values in the literature were determined at 254 nm and polychromatic irradiation was used in the present study, we can exclude a wavelength dependent photoreaction.

The degradation of chlorotriazines by sunlight is still a matter of controversy. The intensity of the Xe lamp with Duran jacket and additional optical filter used in this study is comparable to the annual mean sunlight intensity in Europe[45]. Using the sun-like light source for terbuthylazine a half-life of more than 1 month can roughly be estimated in agreement with a reported measurement in natural sunlight ($t_{1/2} \approx 3$ months[39]). However, for very high sunlight intensities a half-life of only 39 h was found[17] (full midday sunlight, latitude 40°). These experimental results confirm the demand that absolute wavelength dependent intensities of polychromatic artificial light sources must be known with accuracy.

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