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OH-radical reactivity and direct photolysis of triphenyltin hydroxide in aqueous solution

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Abstract

Photolytic degradation reactions in aqueous solution of the fungicide triphenyltin hydroxide (TPT), a compound with typical physico-chemical properties of a persistent organic pollutant (POP) were investigated. The quantum yield is found to be close to unity, $\Phi_{\mathrm{TPT},254} \pm 2\sigma = 1.25 \pm 0.26$ at 254 nm ($T = 295$–298 K). Using nitrobenzene as reference compound the OH-rate constant of TPT was found to be $k_{\mathrm{OH,TPT}} \pm 2\sigma = (9.4 \pm 3) \times 10^{9}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ at $T = 295$ K. Although the quantum yield of TPT is among the highest values found for a pesticide, the degradation by sunlight is negligible due to a lack of overlap with the UV-spectrum of TPT. Adopting OH-levels of $c_{\mathrm{OH}} = 2.5 \times 10^{-16}$ M the OH-rate constant of dissolved TPT leads to a lifetime of about 1 week in surface waters. However, the lifetime found is assumed to be a minimum value and the influence of the adsorption of TPT on particles on degradation reactions in the environment should be investigated.

Keywords: Triphenyltin hydroxide; Fentin hydroxide; Quantum yield; OH-rate constant; Degradation

1. Introduction

Triphenyltin hydroxide (TPT) is used as a fungicide (common name Fentin hydroxide or with acetate as counter anion Fentin acetate) especially on potato cultures [1]. As for the corresponding tributyltin compound (TBT) TPT is known to be highly toxic [2] and since August 2001 the use of TPT as a pesticide is forbidden in Germany. Although numerous studies were published with concentration profiles of organotins in the aquatic environment [3–5] (for extensive compilations see [2,6] and references therein) rate constants for the reaction by OH-radicals or by direct photolysis to assess the abiotic degradation initiated by light are still missing [7,8].

Two main pathways for the light induced, abiotic degradation of pesticides in the environment in solution [9] (and almost exclusively in the gas phase [10]) are reaction with OH-radicals (with concentration c (M) and OH-rate constant k_{OH} ($\mathrm{M}^{-1}\,\mathrm{s}^{-1}$)) and direct photolysis by sunlight (with in principle wavelength dependent quantum yields, Φ_λ, sunlight intensities, I_λ (einstein $\mathrm{nm}^{-1}\,\mathrm{s}^{-1}\,\mathrm{cm}^{-2}$), and decadic molar absorption coefficients, ϵ_λ ($\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$)), leading to the overall rate constant, k (s^{-1}), summarized in Eq. (1) (see [11] for a discussion):

$$k_{\mathrm{abiotic}} = k_{\mathrm{OH}} \times c + 2303 \sum_{\lambda} I_\lambda \Phi_\lambda \epsilon_\lambda \qquad (1)$$

The hydrolysis of TPT for pH < 5.5 was found to be negligible within 4 days [12] and even within 30 days at 32 °C [13] and the loss of triphenyltin acetate in water within 3 h was interpreted as a reaction to triphenyltin hydroxide [14]. Light induced degradation reactions of tinorganic compounds in aqueous solution were reported for TBT [7,15–18] and TPT [1,13,19]. Furthermore, the influence of titanium dioxide on the photolytic degradation of TBT [20] and TPT [12] and the photolysis of TPT on soil surfaces [14] was investigated. Besides inorganic tin, found as the final product in the photolysis of TPT (via the corresponding intermediates by loss of aryl groups) [12–14,19] phenol [19] and assumed polyphenols [13] were detected. Extremely low quantum yields in aqueous solution for TPT (besides other tinorganic compounds such as TBT) of about 10^{-6} were published [18,19] whereas OH-rate constants of tinorganic compounds are not known. In this study, we present for the first time the determination of the OH-rate constant of TPT and UV-spectra in aqueous solution. Furthermore, the revisited determination of the quantum yield of TPT leads to a value in striking contradiction to published data [19]. Rate constants and

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physicochemical properties were used to discuss the environmental fate of TPT.

2. Experimental setup

2.1. Instrumentation and materials

UV-spectra (double beam spectrometer Lambda 45 with pre-monochromator, Perkin-Elmer) were measured with a resolution of 2 nm in 1 nm steps at $d = 1$ cm and $d = 5$ cm in quartz cuvettes at ambient temperature with the corresponding solvent as reference. The wavelength accuracy has been checked by a holmium filter to be better than $\Delta\lambda = \pm 1$ nm.

Nitrite was analyzed by ion chromatography (Dionex DX 120, with suppressor). For quantum yield measurements of TPT a low pressure mercury light source (Penray) was used which emits light at 254 nm. The distance between the light source and a stoppered quartz cuvette (optical pathlength $d = 1$ cm, irradiated area $A = 2\,\mathrm{cm}^2$, irradiated volume $V = 3.5\,\mathrm{cm}^3$) with the corresponding solution of TPT in water was 5 cm. The cuvette was not thermostated, however temperature of the solution in the cuvette was always between 295 and 298 K. The lamp housing was flushed with nitrogen to avoid the production of ozone by the mercury light source. After a given irradiation time the cuvette was removed and the solution was analyzed by HPLC. Maximum irradiation time using this setup was about 15 min.

For the determination of the OH-rate constant of TPT a photolysis apparatus on an optical bench (Amko, Tornesch, Germany) with a Xe lamp XBO 1000 (1000 W, Osram, German) was used. Light was focused by mirrors through a water filter (equipped with quartz windows) and an optical glass filter into a stoppered quartz cuvette ($d = 1$ cm, $A = 2\,\mathrm{cm}^2$, $V = 3.5\,\mathrm{cm}^3$) with the corresponding solution. The distance between light source and cuvette was 70 cm. The Xe lamp, mirrors and the water filter were cooled by tap water, cooling of the cuvette ($T = 295 \pm 1$ K) was accomplished by a thermostat. The temperature in the cuvette was determined after an equilibration period (1 h) using a standard laboratory thermometer. After a given irradiation time the cuvette was removed and the solution was analyzed by HPLC. Maximum irradiation time using this setup was about 90 min.

Analysis of all organic compounds (TPT, terbuthylazine and the reference compound nitrobenzene) was performed by HPLC (Agilent 1100, quaternary pump, autosampler and DAD detector) with the following parameters: detection wavelength = 220 nm; injection volume = 50 μl (for experiments with terbuthylazine, used as a quality check for the photolysis: 20 μl); flow = 1 ml min^{-1}; column = Eclipse XDB C8, 5 μm (Agilent); gradient using acetonitrile (A) and 0.005 M phosphoric acid (B): 5 min held at 10% A, 3 min linear increase to 60% A, 4 min held at 60% A, 3 min linear decrease to 10% A. Response factors of all compounds were obtained from solutions in methanol with defined concentrations by weighting.

Actinometric measurements with iron oxalate were performed as usual [21] determining the absorbance of Fe(II) with 1,10-phenanthroline at 510 nm ($\epsilon = 11{,}100\,\mathrm{l\,mol^{-1}\,cm^{-1}}$ [22]).

For the preparation of saturated aqueous TPT solutions 10 mg of TPT were stirred overnight in 300 ml of deionized water at room temperature. After precipitation of TPT the upper part of the solution was sucked off. For irradiation experiments 200 ml of this solution was diluted with 20–50 ml of deionized water. Exact concentrations of TPT were always determined by HPLC. For the determination of OH-rate constants the aqueous TPT solutions were diluted with aqueous solutions of sodium nitrate and nitrobenzene leading to $c(\mathrm{NaNO_3}) = 603\,\mathrm{mg\,l^{-1}}$ and c(TPT) and c(nitrobenzene) of 1–3 $\mathrm{mg\,l^{-1}}$, determined by HPLC. Always freshly prepared solutions were used for each experimental run.

Potassium trioxalato ferrate(III) (‘iron oxalate’, Alfa) was recrystallized from methanol, TPT (Ehrenstorfer, Germany, 98%), terbuthylazine (Riedel de Haen, 99%), nitrobenzene (Aldrich, >99%), isopropanol (Merck, >99.7%), sodium nitrate (Merck, >99.5%), phosphoric acid (Merck, p.A., 85%), acetonitrile (Promochem, HPLC gradient grade) and methanol (Baker, HPLC gradient grade) were used as received. Deionized water with a resistivity of 18.4 MΩ cm was produced from a water purification system (Membra Pure, Germany).

2.2. Actinometry and quantum yields

For quantum yield measurements with the monochromatic mercury light source at $\lambda = 254$ nm light intensities $I_{\lambda,\mathrm{abs}}$ (einstein^{-1}) were calculated at 254 nm (Eq. (2)) from the iron oxalate actinometer using the moles iron(II) produced per second, $n_{\lambda,t}$ (mol^{-1}), the quantum yield of iron oxalate, Φ_λ, at 254 nm ($\Phi_{254} = 1.25$, mean value from $\Phi_{254} = 1.22$ [21] and $\Phi_{254} = 1.28$ [23]) and the absorption of iron oxalate, E_λ, at 254 nm:

$$n_{\lambda,t} = \Phi_\lambda I_{\lambda,\mathrm{abs}}(1 - 10^{-E_\lambda}) \tag{2}$$

With the absolute light intensity $I_{\lambda,\mathrm{abs}}$ (einstein s^{-1}) obtained by actinometry, Eq. (2) was also used to calculate the quantum yield of TPT. The absorption, E_λ, of TPT was calculated from the decadic molar absorption coefficient at 254 nm and the start concentration. The moles reacted, $n_{\lambda,t}$, were calculated from the start concentration of TPT and the photolysis-rate constant k (s^{-1}).

To characterize the polychromatic light source used in the determination of OH-rate constants a somewhat more extensive calculation procedure is necessary. Relative light intensities of xenon light sources are comparable above 350 nm, differences result from various glass filters used in the laboratory absorbing especially below 350 nm [24]. Hence, relative polychromatic light intensities, $I_{\lambda,\mathrm{rel}}$ were calculated from the absorbance of the optical glass filter, $E_{\lambda,\mathrm{f}}$, used in the experimental setup and from measurements of the relative light intensities of a typical xenon light source

(XOP7, Philips) [24,25] in 1 nm steps with a quartz filter, $I_{\lambda,\mathrm{q}}$ (Eq. (3)):

$$I_{\lambda,\mathrm{rel}}=I_{\lambda,\mathrm{q}} \times 10^{-E_{\lambda,\mathrm{f}}} \tag{3}$$

Relative and absolute light intensities are connected by a factor F (einstein s^{-1}, Eq. (4)):

$$I_{\lambda,\mathrm{abs}} = F I_{\lambda,\mathrm{rel}} \tag{4}$$

and Eq. (2) expands to Eq. (5)

$$n_{\lambda,t} = \Phi_\lambda F I_{\lambda,\mathrm{rel}}(1-10^{-E_\lambda}) \tag{5}$$

leading to Eq. (6) for a polychromatic light source with n_t (moles iron(II) formed in the wavelength region used), Φ_λ (quantum yield of iron oxalate), $I_{\lambda,\mathrm{rel}}$ (relative light intensities of the light source) and E_λ (absorbance of iron oxalate)

$$n_t = \sum n_{\lambda,t} = F \sum \Phi_\lambda I_{\lambda,\mathrm{rel}}(1-10^{-E_\lambda}) \tag{6}$$

The conversion factor F was calculated in 1 nm steps from Eq. (6) with n_t determined as in the monochromatic case from iron oxalate, $I_{\lambda,\mathrm{rel}}$ from Eq. (3), E_λ by absorption spectroscopy of the iron oxalate solution used and Φ_λ from a polynomial fit using published quantum yields of iron oxalate [21,23,26] in the wavelength region 254–577 nm (Eq. (7)):

$$\Phi_\lambda = 4.10-0.0257\lambda+7.698\times10^{-5}\lambda^2 - 7.773 \times 10^{-8}\lambda^3 \tag{7}$$

2.3. Determination of OH-rate constants

OH-radicals were produced by irradiation of sodium nitrate. The monoexponential loss of the compound with concentrations c (M) and OH-rate constant k_{OH} ($\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) by OH-radicals with concentrations c_{OH} (M) leads to Eq. (8) and for constant OH-radical concentration to Eq. (9):

$$\ln\left(\frac{c_0}{c}\right) = k_{\mathrm{OH}}\int_{t_0}^{t} c_{\mathrm{OH}}\,\mathrm{d}t \tag{8}$$

$$\ln\left(\frac{c_0}{c}\right) = k_{\mathrm{OH}}\overline{c_{\mathrm{OH}}}t = kt \tag{9}$$

Eqs. (8) and (9) hold for TPT as the compound in interest and nitrobenzene (NB), chosen as a reference compound with known OH-rate constant ($k_{\mathrm{OH,NB}} = 3.9\times10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ [27,28]). Hence, the OH-rate constant of TPT ($k_{\mathrm{OH,TPT}}$, $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) can be calculated from Eq. (10) or for constant OH concentration from Eq. (11):

$$\ln\left(\frac{c_{\mathrm{TBT},0}}{c_{\mathrm{TBT}}}\right) = \frac{k_{\mathrm{OH,TPT}}}{k_{\mathrm{OH,NB}}}\ln\left(\frac{c_{\mathrm{NB},0}}{c_{\mathrm{NB}}}\right) \tag{10}$$

$$k_{\mathrm{OH,TPT}} = k_{\mathrm{OH,NB}}\frac{k_{\mathrm{TPT}}}{k_{\mathrm{NB}}} \tag{11}$$

In this study, OH-radical concentrations were found to be constant and the OH-rate constant of TPT was therefore calculated from Eq. (11).

3. Results and discussion

3.1. Analysis of TPT and nitrobenzene

Aqueous solutions of TPT were analyzed relative to known concentrations of TPT in methanol. For all analytical runs, chromatograms of blank samples (water or methanol) were subtracted from the corresponding chromatograms of samples with the compounds in interest. HPLC-areas for aqueous solutions of TPT diluted with water were found to be strictly linear (correlation coefficient $R > 0.9999$) in the concentration range of 1.4 mg l^{-1} down to 50 μg l^{-1} ($c = 1.36 \times 10^{-7}$ mol l^{-1}) leading to a response factor of $R(\mathrm{TPT}) = 124.4$ areas l mg^{-1} at 220 nm with a retention time of $\mathrm{RT(TPT)} = 8.22$ min. The same holds for nitrobenzene (correlation coefficient $R > 0.999$) with a response factor of $R(\mathrm{NB}) = 92.9$ areas l mg^{-1} at 220 nm and a retention time of $\mathrm{RT(NB)} = 9.67$ min. A typical HPLC-chromatogram of a mixture of TPT, nitrobenzene and sodium nitrate used in the determination of the OH-rate constant of TPT is shown in Fig. 1. The corresponding response factor of terbuthylazine, used as a quality check for photolysis experiments at 254 nm was $R(\mathrm{terbuthylazin}) = 174.3$ areas l mg^{-1} at 220 nm with a retention time of $\mathrm{RT(terbuthylazine)} =$ 12.05 min.

Aqueous solubility of TPT, obtained from saturated aqueous solutions was found to be $S(TPT) \pm 2\sigma = 2.6 \pm 0.3$ mg l^{-1}.

We were especially interested in precise kinetic information on TPT besides other compounds as nitrobenzene without clean-up of the corresponding solutions. With the analytics used it is not possible to determine the monophenyltin cation (MPT) and diphenyltin cation (DPT), reported to be the degradation products of TPT in photolysis experiments [19]. We also have investigated triethyl amine in the eluent to separate mono- and diphenyltin from triphenyltin or in addition tropolone to separate all the three phenyltin compounds [29]. However, the absorption of triethylamine in the eluent excludes observation wavelengths below 250 nm. The necessity to use the much lower absorption band around 260 nm to detect TPT leads to much higher detection limits of TPT of about 0.5 mg l^{-1}. Tropolone totally prevents the UV-detection of TPT due to strong absorption bands of tropolone between 200 and 370 nm. The development of an application using HPLC in connection with ICP-MS is under way.

3.2. UV-spectrum of TPT

For precise measurements of the UV-spectrum of TPT in water an optical path length of 1 cm is not sufficient due to the low solubility of TPT. Hence, UV-spectra in water were measured with an optical path length of 5 cm. UV-spectra of TPT in water (saturated aqueous solution), in methanol and for comparison from the DAD (at 60% acetonitrile/40%

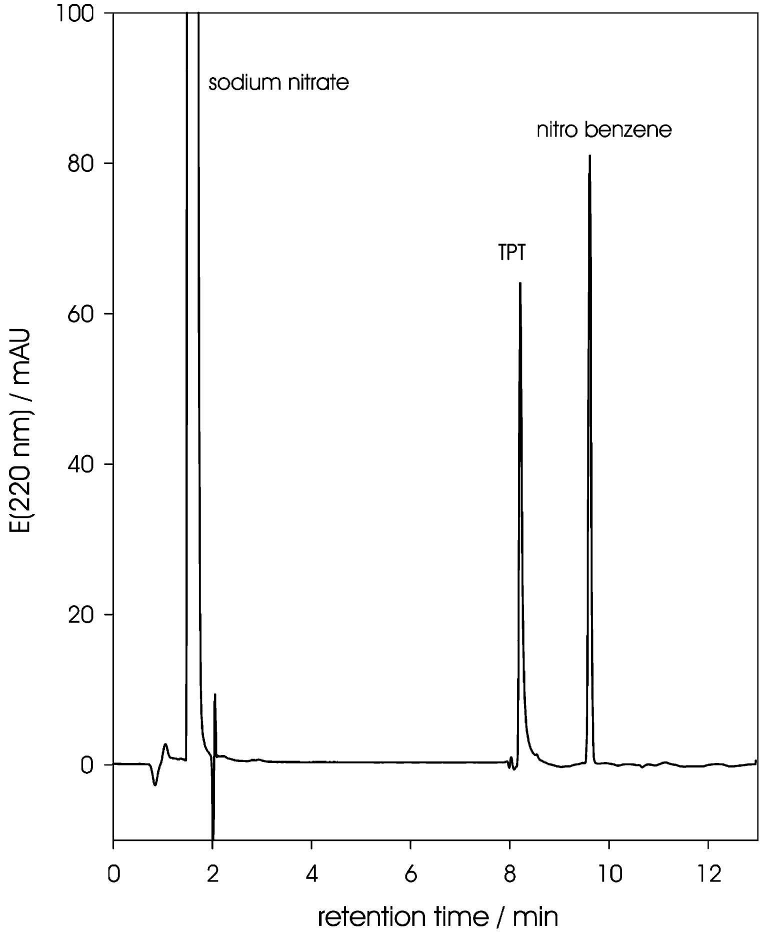

Fig. 1. Typical chromatogram in the separation of sodium nitrate ($c = 7.09 \times 10^{-3}$ M, RT = deadtime), TPT ($c = 6.11 \times 10^{-6}$ M, RT = 8.22 min) and nitrobenzene ($c = 2.78 \times 10^{-5}$ M, RT = 9.67 min). HPLC conditions are described in the text.

0.005 M phosphoric acid) normalized to the water spectrum at 257 nm are shown in Fig. 2.

Molar absorption coefficients were calculated from known concentrations by weighting (methanol) and from analysis by HPLC (water). Five maxima in the first electronic band of TPT around 260 nm were found with the following molar absorption coefficients obtained from saturated aqueous solutions (λ, nm (ϵ, $M^{-1}\,cm^{-1}$)): 246 (474); 251 (591); 257 (710); 262 (474); 268 (328). A molar absorption coefficient at the irradiation wavelength 254 nm of $\epsilon = 554\,M^{-1}\,cm^{-1}$ was used in the calculation of the quantum yield (for comparison in methanol: $\epsilon_{254} = 582\,M^{-1}\,cm^{-1}$). Due to the low absorptions and the error in the solubility of TPT the accuracy of the molar absorption coefficients is predicted to be not better than 10%. UV-spectra of TPT always show a tail above 275 nm by unknown impurities, leading to uncertain molar absorption coefficients for $\epsilon < 10\,M^{-1}\,cm^{-1}$. The normalized UV-spectrum obtained by the DAD from the peak of TPT in the HPLC-chromatogram shows no shoulder or a tail down to $\epsilon < 1\,M^{-1}\,cm^{-1}$ which proves a negligible absorption of TPT above 285 nm. Hence, there is practically no overlap between the UV-spectrum of TPT in water and typical sunlight intensities [30,31] (for a discussion see also [25] and Fig. 3) and therefore the degradation of TPT by direct sunlight photolysis is negligible.

Within the error of the experiment no differences of the UV-spectra of TPT with respect to a wavelength shift or a change in molar absorption coefficients at pH-values between 2 and 14 were found. These experiments were especially performed to measure the pK_A of TPT, reported to be pK_A(TPT chloride) = 5.48 [32]. Therefore, UV-spectroscopy failed in this case for TPT to be a suitable method to measure the pK_A.

3.3. Quantum yield of TPT at 254 nm

The absolute light intensity of the mercury light source at 254 nm, obtained from five different irradiation times between 1 and 5 min, was found to be $I_{254,abs} \pm 2\sigma = (3.69 \pm 0.37) \times 10^{15}$ photons s^{-1}. Two different photolysis experiments of TPT at 254 nm were performed at 15 different irradiation times with a maximum conversion of 93% for TPT. For both irradiation experiments a monoexponential loss of TPT was found (Fig. 4).

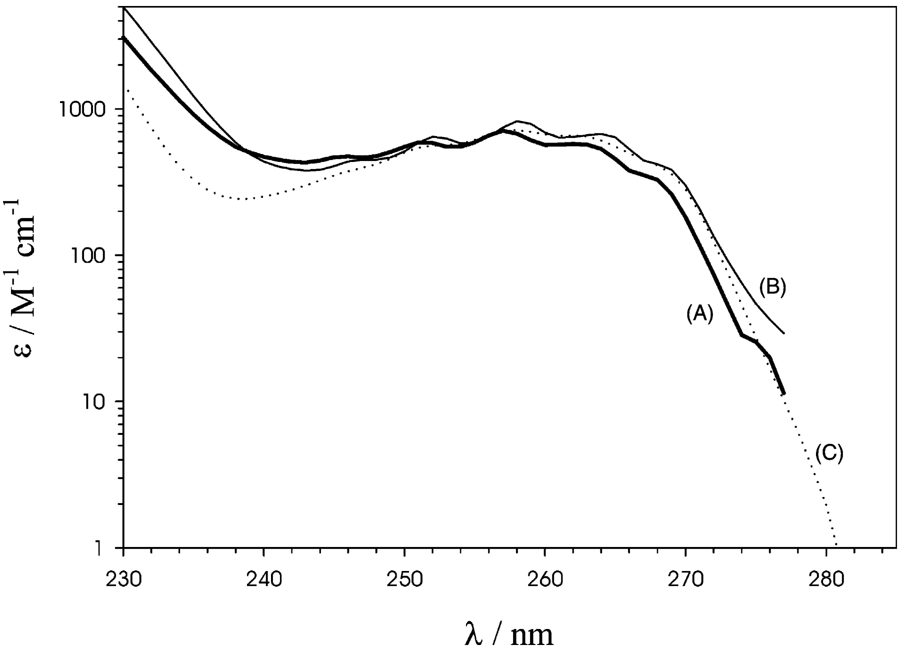

Fig. 2. UV-spectra of TPT: (A) in water, (B) in methanol, (C) HPLC-DAD, normalized to the UV-spectrum in water at 257 nm.

Combining both irradiation experiments the photolysis-rate constant determined under the conditions used was $k \pm 2\sigma = (2.8 \pm 0.3) \times 10^{-3}\,\mathrm{s}^{-1}$. A surprisingly high discrepancy of 28% of the start concentration in both irradiation experiments ($c_0 \pm 2\sigma = (4.3 \pm 0.3) \times 10^{-6}\,\mathrm{M}$) in comparison with the start concentration from linear regression of the logarithmic concentrations versus time ($c'_0 \pm 2\sigma = (3.1 \pm 0.3) \times 10^{-6}\,\mathrm{M}$ from the intercept of Fig. 4) was found. However, additional blank experiments in the dark with aqueous solutions of TPT in quartz cuvettes lead to no loss of TPT within the error of the analytical measurement (±7%). An explanation for the loss of TPT at start of the photolysis is still missing and start concentrations were not used in the calculation of the photolysis-rate constant. Using the moles of TPT converted per second in the beginning of the reaction (calculated from the photolysis-rate

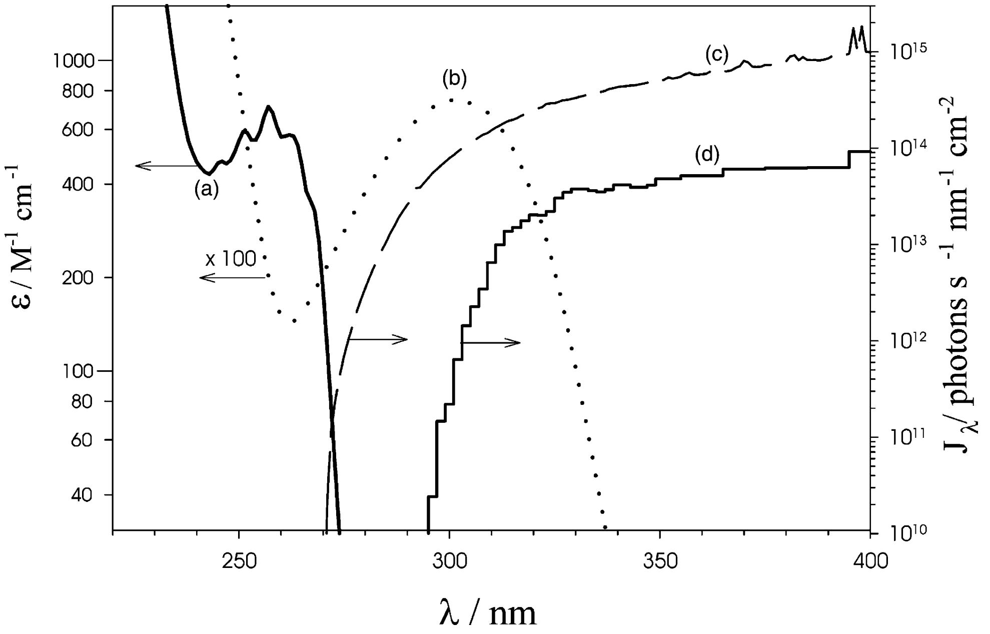

Fig. 3. Comparison of (a) the UV-spectrum of TPT, (b) the UV-spectrum of sodium nitrate, (c) the absolute light intensities of the polychromatic light source used, and (d) calculated sunlight intensities for middle Europe (latitude 50°) [31].

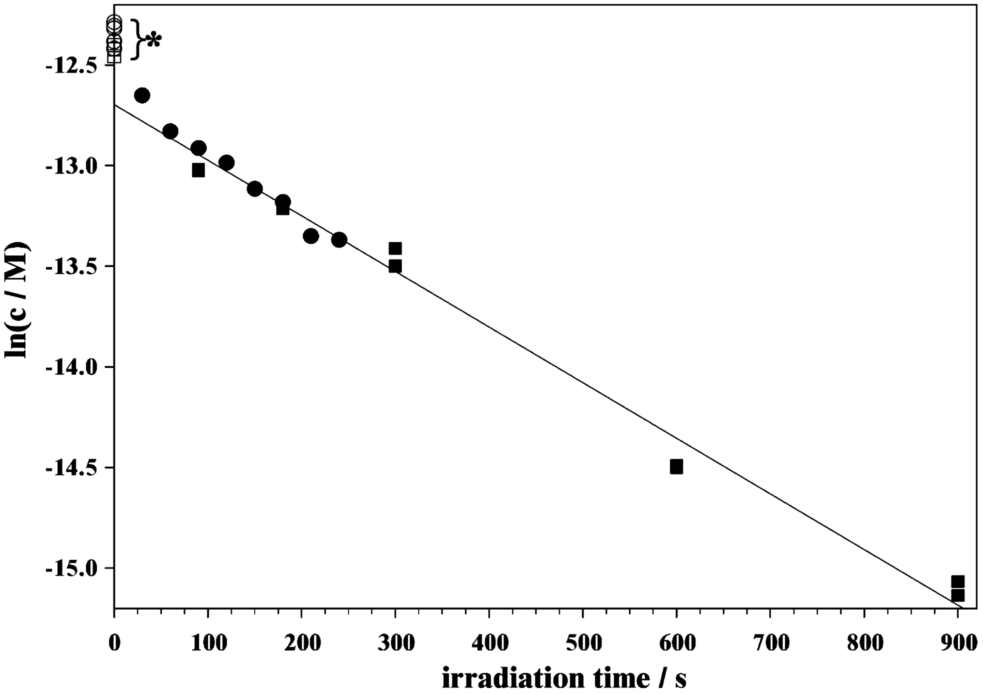

Fig. 4. Plot of the logarithmic (base e) concentrations vs. time in the photolysis of TPT at 254 nm for two independent irradiation experiments (circles and squares). Start concentration (marked by an asterisk) obtained by HPLC at $t = 0$ was $(c_0 \pm 2\sigma) = (4.25 \pm 0.30) \times 10^{-6}$ mol l^{-1}, conversion of TPT at $t = 900$ s was 93%. Linear regression was performed without concentrations at $t = 0$ leading to a photolysis-rate constant of $(k \pm 2\sigma) = (2.8 \pm 0.3) \times 10^{-3}$ s^{-1} and an intercept of $(c'_0 \pm 2\sigma) = (2.8 \pm 0.3) \times 10^{-3}$ s^{-1}. See text for a discussion of the discrepancy between measured start concentration and start concentrations obtained by linear regression and the corresponding influence on the calculation of the quantum yield.

constant, the start concentration and the irradiation volume $V = 3.5$ ml) and the absorption at 254 nm ($E_0 = 0.00235$, calculated from the molar absorption coefficient and the start concentration) and the absolute light intensity obtained by actinometry, a quantum yield of $\Phi = 1.25$ was found. The propagation of error using errors of 7% in concentration, 10% in light intensities, 10% in molar absorption coefficient and 11% in the photolysis-rate constant leads to an overall error of $\Delta\Phi = 0.26$, hence

$$\Phi_{\mathrm{TPT},254} \pm 2\sigma = 1.25 \pm 0.26$$

Due to the low concentrations used the uncertainty of the start concentration is practically negligible in the calculation of the quantum yield. The maximum possible quantum yield of about 1 for TPT found in this study is in striking contradiction to a published extremely low quantum yield for the chloride of TPT in water ($\Phi = 1.12 \times 10^{-6}$ [19]). We therefore have performed three additional series of experiments.

In the first photolysis experiment we have used a 10% acetonitrile/water solution of the pesticide terbuthylazine ($c_0 = 3.05 \times 10^{-5}$ M, $\epsilon_{254} = 3124$ M^{-1} s^{-1}) to check the photolysis apparatus used and calculated from five different irradiation times (photolysis-rate constant $k = 6.4 \times 10$ s^{-1}) a quantum yield of $\Phi = 0.056$ in agreement with published values ($\Phi = 0.06$ in water/5% CH_3CN from a polychromatic irradiation [24] and $\Phi = 0.094$ in water at 254 nm [33]):

$$\frac{k_{\mathrm{terbuthylazine}}}{k_{\mathrm{TPT}}} = \frac{\Phi_{\mathrm{terbuthylazine}}}{\Phi_{\mathrm{TPT}}} \frac{\epsilon_{254,\mathrm{terbuthylazine}}}{\epsilon_{254,\mathrm{TPT}}} \qquad (12)$$

In the second additional experiment, we photolyzed at 254 nm a mixture of terbuthylazine ($c_0 = 9.08 \times 10^{-6}$ M) with TPT ($c_0 = 2.26 \times 10^{-5}$ M) in 10% acetonitrile/water at six different irradiation times. A quantum yield of $\Phi_{\mathrm{TPT}} \approx 0.4$ was estimated using Eq. (12) [34] from the photolysis-rate constants found ($k_{\mathrm{terbuthylazine}} = 0.108$ min^{-1} and $k_{\mathrm{TPT}} = 0.134$ min^{-1}). It should be noted, that experimentally determined start concentrations of TPT were again higher in comparison to the concentrations obtained from linear regression, as discussed above.

In addition, due to the high concentration used ($c > 2$ M) acetonitrile acts as a scavenger for OH-radicals ($k_{\mathrm{OH}} = 2.2 \times 10^7$ M^{-1} s^{-1} [28]) and we therefore exclude a major influence by OH-radicals in the photolytic degradation of TPT under the conditions used.

In the third experiment, we used the polychromatic xenon light source without any additional optical filter to photolyze TPT. The light intensity of the xenon light source below 280 nm is highly uncertain (see discussion above) and experiments were performed to get a very rough estimation of the potential to photolyze TPT. An estimated quantum yield of $\Phi \approx 0.3$ was found for TPT in aqueous solution using this uncertain light intensity in sufficient agreement with the precise value obtained at 254 nm.

As for TPT [19] the same group reported quantum yields for MPT and DPT [19] and for corresponding butyltin chlorides [18] in the range of $\Phi = (1–12) \times 10^{-6}$. The discrepancy of the quantum yield of TPT found in this study and the reported extremely low quantum yields is unresolved. Properties of organotin compounds are known to be relatively independent on the counter anion (such as hydrolysis [35], pK_A [32] or toxicity [15]) and we therefore exclude such a strong difference in quantum yields for the hydroxide of TPT (this study) and the chloride of TPT [19].

However, although results found in this study are in contradiction to the general statement that 'phenyltin species offer high resistance to photodegradation' [19], in particular this is true for the photolysis of aqueous solutions of TPT by sunlight in the environment. Although the quantum yield of TPT is high, the reason of the stability of TPT with respect to photolysis in the environment is the practically not existing overlap of the UV-spectrum of TPT and typical sunlight spectra (see Fig. 3). The high quantum yield of TPT has further implications on the transferability of photolysis experiments performed in the laboratory to environmental conditions. Quantum yields, always determined in laboratory experiments, and detailed UV-spectra are often missing for environmentally relevant compounds, in particular for aqueous solutions. Both properties are necessary to assess the potential photolysis in the environment. Uncertain relative light intensities in qualitative photolysis studies performed in the laboratory result in erroneous assessments of the photolysis of compounds with high quantum yields and UV-spectra with electronic bands near the edge of the sunlight spectrum (i.e. around 290 nm, see also discussion in [9]). This is especially true for TPT, a compound with, to our knowledge, the highest quantum yield for a pesticide known so far.

3.4. OH-rate constant of TPT

Sodium nitrate is a common OH-precursor used in the laboratory [36–38] and known to be relevant in the environment [39–41] in the production of OH-radicals ($\Phi_{OH} = 0.017$ at $\lambda = 308$ and 351 nm and $T = 298$ K [42]). Usually, OH-rate constants are obtained relative to a compound with well known OH-rate constant. Benzoic acid, a reference compound successfully used in light induced degradation reactions of nitrophenols [43,44], was rejected due to stability and analytical problems. We used nitrobenzene instead [41], a stable reference compound with negligible degradation by direct photolysis [41], easy to analyze under the conditions used and with a well defined OH-rate constant in aqueous solution ($k_{OH,NB} = 3.9 \times 10^9\ M^{-1}\ s^{-1}$ [27,28]).

Aqueous solutions were used with high concentrations of sodium nitrate ($603\ mg\ l^{-1} = 7.09 \times 10^{-3}$ M) and

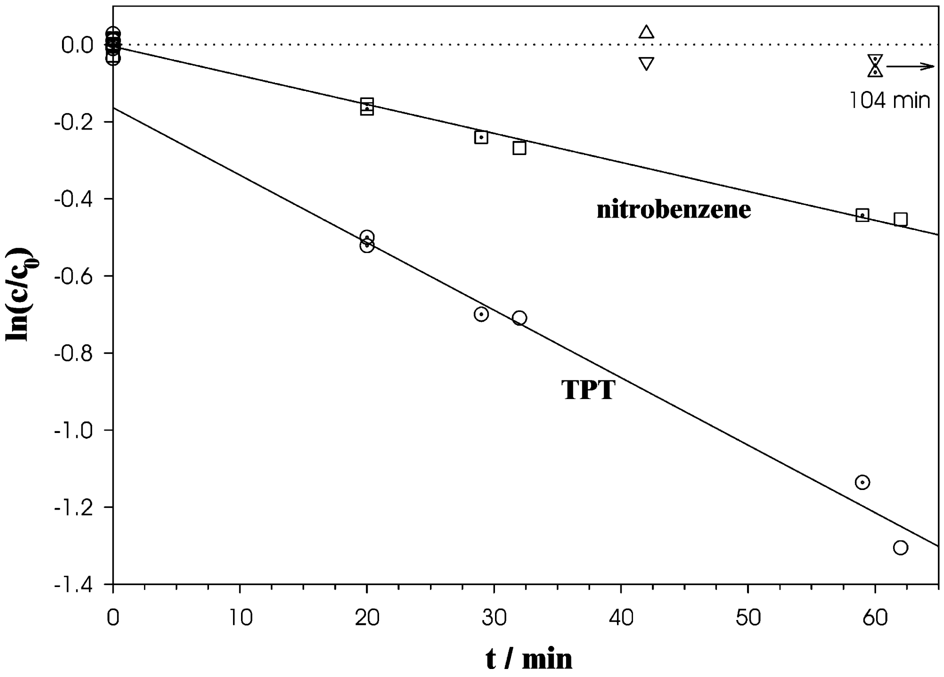

Fig. 5. Plot of the logarithmic (base e) concentration ratios (c/c_0) vs. time in the reaction of TPT and nitrobenzene by OH-radicals (photolysis of $603\ mg\ l^{-1}$ sodium nitrate) for two independent irradiation experiments (TPT: open and dotted circles, $c_0 = 6.38 \times 10^{-6}$ M; nitrobenzene: open and dotted squares, $c_0 = 4.03 \times 10^{-5}$ M). Rate constants from linear regression (solid lines): $k(\text{TPT}) \pm 2\sigma = (0.018 \pm 0.005)\ min^{-1}$, data for $t = 0$ min not included; $k(\text{nitrobenzene}) \pm 2\sigma = (0.0075 \pm 0.0008)\ min^{-1}$. The dotted line represents no degradation. Also included are concentration ratios found in experiments with additional isopropanol (TPT: triangle up; nitrobenzene: triangle down) and without sodium nitrate (TPT: dotted triangle up; nitrobenzene: dotted triangle down). Within an error of 7% no degradation was found in both cases for TPT and nitrobenzene.

concentrations of $c_0 = 6.38 \times 10^{-6}$ M for TPT and $c_0 = 4.03 \times 10^{-5}$ M for nitrobenzene. Results for two independent experimental runs are shown in Fig. 5.

As found in the photolysis experiments start concentrations of TPT were higher (by about 15%) in comparison to the start concentration found as intercept from linear regression. Hence, linear regression for TPT was performed without the experimentally determined start concentrations. The rate constants found are $k(\mathrm{TPT}) \pm 2\sigma = (0.018 \pm 0.005)\,\mathrm{min}^{-1}$ and $k(\mathrm{nitrobenzene}) \pm 2\sigma = (0.0075 \pm 0.0008)\,\mathrm{min}^{-1}$. From these rate constants and with the OH-rate constant of nitrobenzene we calculated from Eq. (11) the OH-rate constant of TPT:

$$k_{\mathrm{OH,TPT}} \pm 2\sigma = (9.4 \pm 3) \times 10^{9}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$$

Hence, the OH-rate constant of TPT is, as usual for most aromatic compounds [27,28] at the diffusion limit. Within the error of the analytical setup no degradation was found for TPT in additional photolysis experiments with isopropanol ($k_{\mathrm{OH,isopropanol}} = 1.9 \times 10^{9}\,\mathrm{M}^{-1}\mathrm{s}^{-1}$ [27,28]) as an OH-radical scavenger and without sodium nitrate (Fig. 5). The monoexponential loss of the reference compound nitrobenzene and the corresponding OH-rate constant leads to a steady-state OH-radical concentration of $\overline{c_{\mathrm{OH}}} \pm 2\sigma = (3.2 \pm 0.4) \times 10^{-14}$ M. As a further criterion to characterize the light source used it is interesting to compare the steady-state OH-concentration obtained from the loss of the reference compound with the corresponding value calculated from the source and sink strength of OH-radicals. The light intensity of the Xe light source in the wavelength region 270–575 nm found by actinometry is $I_{\mathrm{abs}} = 7.96 \times 10^{17}$ photons s^{-1}, the wavelength dependent light intensities per cm^2 calculated from Eqs. (3)–(6) are shown in Fig. 3. The UV-spectrum of sodium nitrate is also shown in Fig. 3 ($\epsilon_{301} = 7.18\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ was found to be 6% higher in comparison to published data [45]). Small amounts of nitrite were found during the photolysis of nitrate (after 40 min $1.0\,\mathrm{mg\,l}^{-1}$ and after 80 min $0.8\,\mathrm{mg\,l}^{-1}$). As for the photolysis of nitrate the photolysis of nitrite leads to OH-radicals [46] and nitrite (UV-spectrum taken from [47], quantum yields $\Phi_{\mathrm{OH}} = 0.07$ (at 308 nm) and 0.046 (at 351 nm) at $T = 298$ K from [48], OH-rate constant $k_{\mathrm{OH,nitrite}} = 9 \times 10^{9}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ from [28]) has to be considered in the calculation of the source and sink strength. The source strength for OH-radicals calculated from the overlap of the light intensities of the Xe light source and the UV-spectrum of nitrate and nitrite (between 270 and 410 nm) and the corresponding quantum yields is $\mathrm{source}_{\mathrm{OH}} = 9.05 \times 10^{-9}\,\mathrm{M\,s}^{-1}$ (80% contribution from nitrate). Assuming the sink for OH-radicals mainly by reaction of TPT, nitrobenzene and nitrite leads to $\mathrm{sink}_{\mathrm{OH}} = 3.65 \times 10^{-5}$ (50% from nitrite, 35% from nitrobenzene and 15% from TPT). The steady-state condition $\mathrm{source}_{\mathrm{OH}}/\mathrm{sink}_{\mathrm{OH}}$ leads to $\overline{c_{\mathrm{OH}}} = 2.5 \times 10^{-14}$ M in reasonable agreement with the value obtained from the loss of the reference compound nitrobenzene.

4. Conclusions

The quantum yield and the OH-rate constant found should be used with other physicochemical parameters (see Table 1) to discuss aspects of the abiotic degradation of TPT in the environment.

TPT is used as a fungicide, i.e. released into the environment by spraying TPT especially on potato cultures which could lead to a distribution in the water compartment by leaching or run-off. Furthermore, TPT could be released into the gas phase. The vapor pressure of TPT at $T = 298$ K is estimated to be $p = 2.8 \times 10^{-6}$ Pa (using $p = 4.7 \times 10^{-5}$ Pa at $T = 232$ K [1] with an assumed enthalpy of vaporization of $\Delta H_{\mathrm{vap}} = 90\,\mathrm{kJ\,mol}^{-1}$ [49,50]). The estimated vapor pressure is very low, leading to practically 100% adsorption on aerosols (using the Junge model, see [51] for a discussion of mean aerosol parameters) and a very high Henry's

Table 1
Physicochemical properties of TPT and estimated lifetimes in homogeneous aqueous solution due to reaction by direct photolysis and OH-radicals

Property	Value	Comment
Solubility (S, $\mathrm{mg\,l}^{-1}$)	1.2	pH 7.0 [13]
Solubility (S, $\mathrm{mg\,l}^{-1}$)	6.6	pH 4.2 [13]
Solubility (S, $\mathrm{mg\,l}^{-1}$)	3.4	Water, Fentin acetate [14]
Solubility (S, $\mathrm{mg\,l}^{-1}$)	2.6 (=7.08×10^{-6} M)	$T = 293$–295 K, this work used to calculate H
Vapor pressure (p, Pa)	4.7×10^{-5}	At $T = 323$ K [1]
Vapor pressure (p, Pa)	$\approx 2.8 \times 10^{-6}$	At $T = 298$ K, estimated with $\Delta H_{\mathrm{vap}} = 90\,\mathrm{kJ\,mol}^{-1}$
Henry's law constant (H, $\mathrm{M\,atm}^{-1}$)	$\approx 2.6 \times 10^{5}$	Estimated using $H = S/p$
Acidity constant ($\mathrm{p}K_{\mathrm{A}}$)	5.48	For triphenyltin chloride [32]
Octanol–water partition coefficient ($\log(K_{\mathrm{ow}})$)	2.9–4.4	pH < 6 to pH > 7.4 compilation in [2]
Fraction bound on aerosols (Ψ)	≈0.9–1	Junge-equation, see [51]
Quantum yield (Φ)	1.25	This work, in water at 254 nm
OH-rate constant (k_{OH}, $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$)	9.4×10^{9}	This work, in water
Lifetime (direct photolysis) (τ_{phot})	∞	No overlap with sunlight intensity
Lifetime (OH-radicals) in surface water (τ_{OH}, days)	4.9	$c_{\mathrm{OH}} = 2.5 \times 10^{-16}$ M [40]
Lifetime (OH-radicals) in cloud water (τ_{OH}, h)	0.3	$c_{\mathrm{OH}} = 1 \times 10^{-13}$ M [48]

If not stated otherwise properties are given at room temperature (293–298 K).

law constant ($H \approx 2.6 \times 10^5$ M atm^{-1}, estimated from the ratio of water solubility and vapor pressure, see Table 1). From the high Henry's law constant a very low tendency of TPT to leave the aqueous phase is assumed in agreement of no loss of TPT from the aqueous phase found in volatilization experiments [13]. Furthermore, a direct input of TPT into the gas phase is not likely due to the very low vapor pressure. Using physicochemical and ecotoxicological properties TPT can be classified as a persistent organic pollutant (POP) with a possible distribution by a long range transport adsorbed on aerosols.

The quantum yield of about 1 for TPT in water, obtained at 254 nm, is among the highest values measured for a pesticide. However, due to a lack of overlap of the UV-spectrum of TPT with the sunlight spectrum a degradation of TPT by direct photolysis is negligible in the environment. Independent, additional photolysis experiments were performed which unequivocally prove the finding of a quantum yield near unity. The discrepancy with a much lower published quantum yield of TPT [19] is still unresolved. The OH-rate constant was found to be at the diffusion limit, as usual for most aromatic compounds. Hence, a rate-decreasing influence by the substituent tin on the reactivity of the aromatic part with respect to OH-radicals was not found. The lifetime of TPT due to reaction with OH-radicals, dissolved in the aqueous phase of surface waters, is estimated to be about 1 week (Table 1). We have also included in Table 1 the lifetime of TPT in cloud water with a much shorter lifetime due to much higher OH-radical concentrations. Nevertheless, as discussed above, a direct release of TPT to the gas phase is not likely (and attempts to measure TPT directly in the gas phase were to our knowledge not performed) and corresponding concentrations in cloud water should be negligible. OH-rate constants in the gas phase of TPT and related tinorganic compounds are not known. Using classical arguments from organic chemistry the neighboring carbons of the tin atom should have a partial negative charge increasing the OH-rate constant of the electrophilic OH-radical (with respect to benzene). Hence, the OH-rate constant in the gas phase should be at least as high as for benzene ($k_{OH} = 1.23 \times 10^{-12}$ cm^3 s^{-1} at $T = 298$ K [52]) in agreement with a few known experimental values for organic mercury and lead compounds [52]. However, pure gas-phase experiments of TPT at 298 K are assumed to be impossible and not important to assess the degradation of TPT in the environment (see discussion above).

As for all semivolatile compounds practically no quantitative values are known of the degradation in the much more important adsorbed state. This holds for TPT adsorbed especially on humic acids in surface waters and on aerosols in the gas phase. Lifetimes obtained for the dissolved state are assumed to be minimum values and experiments to investigate the degradation of TPT in the presence of humic acids in aqueous solutions are under way.

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