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Photoinduced degradation by iron(III): removal of triphenyltin chloride from water

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The photoredox process taking place in iron(III) aquacomplexes was used to cause the complete degradation of triphenyltin (TPT). TPT elimination was proved to come only from attack by hydroxyl radicals generated upon irradiation at 365 nm of $Fe(H_2O)_5OH^{2+}$, the iron(III) species present under the experimental conditions ([Fe(III)] in the range (3–6) × 10^{-4} mol l^{-1}). The first step is the formation of an adduct between hydroxyl radicals and the benzene ring. The main process is a stepwise dephenylation of the starting TPT. Hydroxylated phenyltin derivatives were also formed, but only as minor photoproducts. The process was shown to be efficient with artificial light as well as with solar light. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: triphenyltin; photodegradation; iron(III); aqueous solution; hydroxyl radicals; mineralization

During recent decades, interest in many countries in the environmental chemistry of organotin compounds has increased dramatically. The reason for the increased awareness of the environmental aspects of organotins is due primarily to the high toxicity of organotin compounds and to the wide range of industrial applications discovered for organotin chemicals. Although inorganic tin compounds generally have very low toxicity, some organotins are very toxic to both animal and vegetable life.[1] The highest toxicity is observed in triorganotin compounds, while di- and mono-organotin compounds show successively lower toxicity.

In the European Community, triphenyltin (TPT) is included in list I of the Council Directive 76/464, which covers dangerous substances to be removed from discharges. TPT is used as an antifouling agent in boat paints, as pesticides in agricultural applications, as biostabilizers for plastics (PVC and PUR), and as fungicides in the wood industry.

The environmental fate of TPT in natural water has been studied. In 1995, Fent and Hunn[2] concluded that TPT is persistent in harbour sediments with a residence time of more than a decade, and that sediments act as a sink and reservoir, but also as potential sources of these compounds. Moreover, contamination of river systems strongly indicates that the occurrence of organotins in surface waters is still widespread, and that degradation in sediments is a very slow process.

Among the different abiotic degradation processes, solar irradiation is one of the main factors responsible for TPT degradation in the environment. TPT was shown to be photodegraded to diphenyltin (DPT) by solar light or UV light[3] and, more recently, Navio *et al.*[4] have shown that the UV-photoassisted degradation of TPT in water takes place by sequential dephenylation *via* DBT and monophenyltin (MPT). They identified some photoproducts and estimated the quantum yield Φ of TPT disappearance, in their conditions, as equal to 1.12×10^{-6}. Because of the very low value of Φ, degradation of TPT was investigated by the action of powdered TiO_2 under UV illumination in aqueous solution.[5] However, the rate constant for the photodegradation of TPT in the presence of TiO_2 is slightly lower than in the absence of the catalyst.

Degradation of several water pollutants photoinduced by iron(III) has been studied in our laboratory.[6–9] The process is based on the formation of hydroxyl radicals and iron(II) upon irradiation of iron(III) aquacomplexes. The reoxidation of iron(II) into iron(III) gives rise to its continuous formation of hydroxyl radicals leading to complete mineralization of

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the pollutant. In all cases, we concluded that degradation photoinduced by iron(III) was an interesting process for the elimination of pollutant in aqueous solution. Recently, we published a paper on the degradation of tributyltin chloride; the main route of tributyltin degradation was a stepwise debutylation.[10]

In the work reported here, we investigated the degradation of TPT photoinduced by iron(III) in aqueous solution. We studied the photodegradation process of TPT via kinetic and analytical approaches. Some intermediate products were identified. The environmental aspect has been studied; we also used sunlight irradiation and we checked the total removal of TPT and these photoproducts.

MATERIALS AND METHODS

Reagents and solutions

TPT chloride (95%), DPT dichloride (96%), MPT trichloride (98%), and tin(IV) chloride pentahydrate (>98%) were purchased from Aldrich. The range investigated in this work was 0–2 ppm, which corresponds to $(0–1.7) \times 10^{-5}$ mol l^{-1} as organotin derivative. These solutions were generally prepared by mixing a saturated TPT aqueous solution for 1 day and the required concentration was obtained by dilution in water. The calibration curve was realised by gas chromatography (GC) equipped with a flame ionization detector (FID) with different solutions obtained by diluting stock solution of organotins prepared in acetonitrile (Carlo Erba reagent, HPLC grade) at 100 mg of tin per litre (100 ppm) with water. The use of methanol was prohibited owing to its role as a hydroxyl radical scavenger.

Ferric perchlorate nonahydrate ($Fe(ClO_4)_3 \cdot 9H_2O$; >97%) and barium hydroxide octahydrate (≥98%) were Fluka products and were kept in a dessicator. The iron(III) solutions for the studies were prepared by diluting stock solutions [2.0×10^{-3} mol l^{-1} in $Fe(ClO_4)_3 \cdot 9H_2O$] to the appropriate iron(III) concentration. Sodium tetraethylborate ($NaBEt_4$; minimum 98%) was a Strem Chemical product kept at 6 °C and under argon. The solutions were prepared by dissolving 20 mg of $NaBEt_4$ in 1 cm^3 of deionized water. 8-Hydroxyquinoline-5-sulfonic acid monohydrate (HQSA; 98%) was purchased from Aldrich. Isooctane and isopropanol were Merck products (HPLC grade).

All solutions were prepared with deionized ultrapure water ($\rho = 18.2$ MΩ cm). When necessary, the solutions were degassed by bubbling with argon for 45 min at room temperature. The pH was measured with an ORION pH meter to ± 0.02 pH unit [pH 3.3 for a solution with a concentration in iron(III) equal to 3.0×10^{-4} mol l^{-1}]. The ionic strength was not controlled.

Apparatus

In order to measure the quantum yields, monochromatic irradiation at 365 nm was carried out with a high-pressure mercury lamp (Osram HBO 200 W) equipped with a grating monochromator (Bausch and Lomb). The beam was parallel and the reactor was a cylindrical quartz cell of 10 cm path length. The light intensity $I_{0\ 365\ nm}$ was measured by ferrioxalate actinometry:[11] $I_{0\ 365\ nm} \approx 3.2 \times 10^{15}$ photons $s^{-1}\ cm^{-2}$.

The apparatus for irradiation of larger volumes at $\lambda_{exc} = 365$ nm was an elliptical stainless steel cylinder. A high-pressure mercury lamp (Philips HPW type 125 W), where emission at 365 nm was selected by an inner filter, was located at a focal axis of the elliptical cylinder. The reactor, a water-jacketed Pyrex tube (diameter: 2.8 cm), was centred at the other focal axis. The reaction medium was well stirred. The unit delivered an actual intensity $I_a \approx 3.20 \times 10^{15}$ photons $s^{-1}\ cm^{-3}$, for 60 ml.

Solar irradiations were carried out in a Pyrex cylindrical reactor during summertime in Clermont-Ferrand, France (latitude 46 °N, 400 m above sea level). UV–visible spectra were recorded on a CARY 3 double beam spectrophotometer.

Gas chromatographic analysis was performed using a DELSI GC DI 700 equipped with an FID. A DB-1 capillary column (dimethylpolysiloxane phase, J&W Scientific, Folson, CA, USA) of dimension 30 m × 0.25 mm i.d. with a film thickness of 0.25 μm was used. Nitrogen carrier gas was used at a flow rate of 1 ml min^{-1}. Samples (2 μl) were introduced onto the column in the splitless injection mode with splitless times of 1 min. The injector temperature was 290 °C and the FID temperature was 280 °C.

GC–mass spectrometry (MS) analysis was performed using a Hewlett Packard model 5985 gas chromatograph–mass spectrometer system. An Optima 5 (Macherey–Nagel) capillary column, dimensions 25 m × 0.25 mm i.d. with a film thickness of 0.25 μm, was used. The injector temperature was 250 °C and the sample was injected in the splitless injection mode for 1 min. Standard EI (70 eV) conditions were used with a source temperature of 250 °C, the mass range being from 20 to 500 m/z units. Helium was used as a carrier gas.

In all GC analyses, the GC oven temperature was maintained at 70 °C for 1 min and increased at 20 °C min^{-1} to a maximum of 270 °C, where it was held for 5 min.

Analysis

Organotin compounds were analysed after reaction of ethylation/extraction as described by Carlier-Pinasseau *et al.*[12] Sodium tetraethylborate was used as an alkylation reagent. Ethylation and extraction of organotin compounds can be performed in water in a one-step procedure. A 165 ± 10 cm^3 Pyrex flask with a narrow neck was used for this operation; 50 ml of water and 200 μl of sodium tetraethylborate at 2% were introduced and the pH was then adjusted to 4.5 using an appropriate quantity of sodium acetate and acetic acid buffer. Isooctane (0.5 ml) was then added and vigorous swirling was obtained by magnetic stirring (1250 rpm for 40 min). The swirling was then

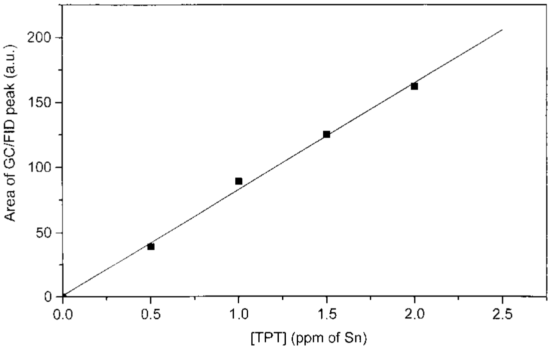


Figure 1. Calibration curve of TPT by GC-FID after derivatization.

stopped and the organic phase transferred into a vial for injection into the gas chromatograph. In these conditions it was possible to identify inorganic tin, MPT and DPT but not to quantify them precisely, due to the poor accuracy of their calibration curves.

Repeated injections (four) were carried out to investigate the reproducibility of the peak area in GC-FID. External calibration was performed for TPT in water using concentrations of 0–2 ppm in tin (Fig. 1). The regression coefficient (0.9983) demonstrated a good calibration linearity in the concentration domain investigated. On the contrary, the calibration curves of DPT and MPT have poor calibration linearity in the same domain of concentration. However, these curves were used to estimate roughly the concentration of DPT and MPT. The concentrations of the oxidized derivatives were also estimated from the calibration curves of the corresponding phenyltin.

The method of measuring the monomeric concentration of iron(III) [i.e. $Fe(OH)^{2+}$] was modified from Kuenzi's procedure.[13] The measurement is based on the formation of the complex $Fe(HQS)_3$ between the HQSA and the iron(III) monomeric species which presents a maximum at 572 nm with a molar absorption coefficient equal to 5075 l $mol^{-1}\,cm^{-1}$.[10]

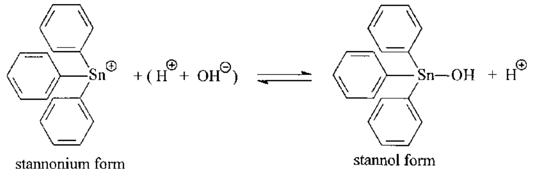
The carbon dioxide (CO_2) produced was determined as $BaCO_3$. It was swept out of the reactor by a flow of oxygen [relieved from CO_2 traces by bubbling in concentrated $Ba(OH)_2$ solution] and trapped in two consecutive $Ba(OH)_2$ solutions at 6.7×10^{-3} mol l^{-1}. The solutions were collected, $BaCO_3$ was allowed to precipitate and the excess of $Ba(OH)_2$ was titrated with a 0.020 mol l^{-1} HCl solution. A blank experiment was performed under the same conditions but without irradiation of TPT.

RESULTS

All organotin concentrations are expressed as tin (mg l^{-1} or ppm). The initial concentration of iron(III) in the solution was generally 3.0×10^{-4} mol l^{-1}.

Characterization of TPT and iron(III) in aqueous solution

TPT is only slightly soluble in water: the maximum solubility is 1.2 ppm at pH 7–9 and 6.6 ppm at pH 4.2.[3] The TPT concentration of the initial solutions used in this work was approximately 2 ppm (pH 5.9 ± 0.1); there was no degradation of TPT when the solution was kept in the dark at room temperature. TPT is stable in aqueous solution. It is better described as a stannol derivative:



TPT absorbs in the ultraviolet region with a maximum at 256 nm ($\varepsilon_{max} = 900$ l $mol^{-1}\,cm^{-1}$) and with a shoulder at 219 nm ($\varepsilon = 30000$ L $mol^{-1}\,cm^{-1}$). Figure 2 shows two spectra of TPT in acetonitrile and in aqueous solution. We observe the same maximum near 256 nm, but the shape of the band is different in the two spectra. In water the spectrum presents an absorption tail up to 320 nm, whereas in acetonitrile there is no absorption after 280nm. This observation can explain the phenomenon of degradation by direct photolysis of TPT in water, already reported in the literature.[3]

Under our experimental conditions ($[Fe(III)] = 3.0 \times 10^{-4}$ mol l^{-1} and pH 3.30 ± 0.1), $Fe(OH)^{2+}$ [$Fe(OH)^{2+}$ refers to $Fe(OH)(H_2O)_5^{2+}$] is the predominant monomeric iron(III) hydroxy complex.[14] However, the concentration of monomeric species decreased rapidly after the dissolution of ferric perchlorate in water. The disappearance was attributed to the possible formation of soluble aggregates.[15] It appeared

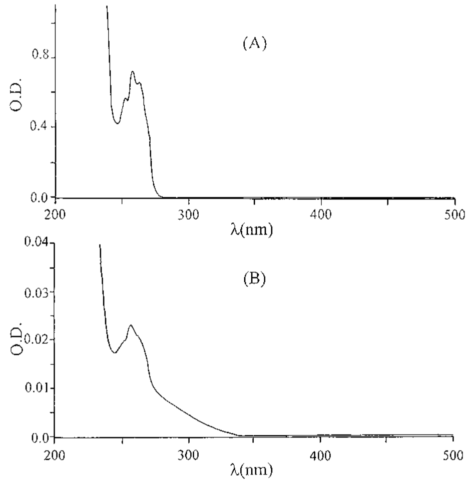


Figure 2. UV–visible spectra of (A) acetonitrile solution of TPT (100 ppm) and (B) aqueous solution of TPT (2 ppm).

that the percentage of $Fe(OH)^{2+}$ strongly depended on the age of the ferric solution and on the starting concentration.[14] By using the HQSA method (see Analysis section) we were able to determine the percentage of $Fe(OH)^{2+}$ in solution:

$$\%Fe(OH)^{2+} = \frac{[Fe(OH)^{2+}]}{[Fe(III)]t_o} \times 100$$

where $[Fe(III)]t_o$ is the starting concentration of total dissolved iron(III). The different percentages of $Fe(OH)^{2+}$ were obtained by the use of iron(III) solutions of different ages. Under our experimental conditions, and unless noted otherwise, the percentage of $Fe(OH)^{2+}$ species represented 80% of the starting iron(III) concentration.

The solution of TPT and iron(III) was stable in the dark at room temperature for a few weeks in terms of TPT concentration. No complexation was observed between TPT and iron(III) in the dark (ground state). The UV–visible spectrum of the TPT and iron(III) mixture was the sum of the individual spectra of TPT and iron(III). The kinetics of $Fe(OH)^{2+}$ disappearance were not affected by the presence of TPT. This is a confirmation of the absence of interaction between TPT and iron(III) in the ground state.

Photoinduced degradation of TPT by iron(III)

The UV–visible spectrum of iron(III) aquacomplexes has an important overlap with solar emission. Consequently, under sunlight, iron(III) aquacomplexes can undergo a photochemical process through an internal electron transfer giving rise to hydroxyl radicals and iron(II):[16]

$$Fe^{3+} + H_2O \xrightarrow{hv} Fe^{2+} + {}^{\bullet}OH + H^+$$

or more precisely in this work

$$Fe(OH)^{2+} \xrightarrow{hv} Fe^{2+} + {}^{\bullet}OH$$

$Fe(OH)^{2+}$ is the most photoactive iron(III) species in terms of hydroxyl radicals production. The rates of pollutant degradation are affected strongly by the $Fe(OH)^{2+}$ percentage in the starting solution.[6,9] Hydroxyl radicals are known to be a very reactive species, reacting with most organic substrates with rate constants that are limited by diffusion. Figure 3A shows a continuous decrease of TPT upon irradiation at $\lambda = 365$ nm. The disappearance of TPT appeared to follow first-order kinetics; a good linear relationship was obtained when plotting $\ln([TPT]_0/[TPT]) = f(\text{irradiation time})$ with $k_{obs} = 0.067\ h^{-1}$ and the half life $t_{1/2}$ is around 10 h (Fig. 3B). The initial quantum yield Φ of TPT disappearance is equal to 0.052.

Irradiation in the presence of 2-propanol

The degradation of TPT can be directly attributed to attack of hydroxyl radicals, as demonstrated by the total inhibition of degradation during irradiation at 365 nm in the presence of 2-propanol (1% v/v), a known hydroxyl radical scavenger; no other radical is generated in the primary process of the degradation.

Influence of oxygen

There was no significant influence of oxygen on the rate of TPT disappearance. We also observed the formation of the same photoproducts with approximately the same stoichiometry.

Photoproduct analysis

Several peaks appeared in the GC-FID chromatogram of an irradiated mixture (Table 1).

The main photoproducts, DPT and MPT, were identified by comparison with authentic samples. DPT and MPT evolutions, as a function of irradiation time at 365 nm, are reported in Fig. 4. DPT and MPT concentrations go through a maximum and then completely disappear for longer irradiation times. Phenol and inorganic tin (identified as $SnEt_4$) were identified by MS and comparison with authentic products. The monohydroxylated derivatives of TPT, DPT and MPT were also identified by GC–MS analysis. These photoproducts (phenol, TPTOH, DPTOH, MPTOH) were present in the irradiated solution at much lower concentrations: two orders of magnitude difference in comparison

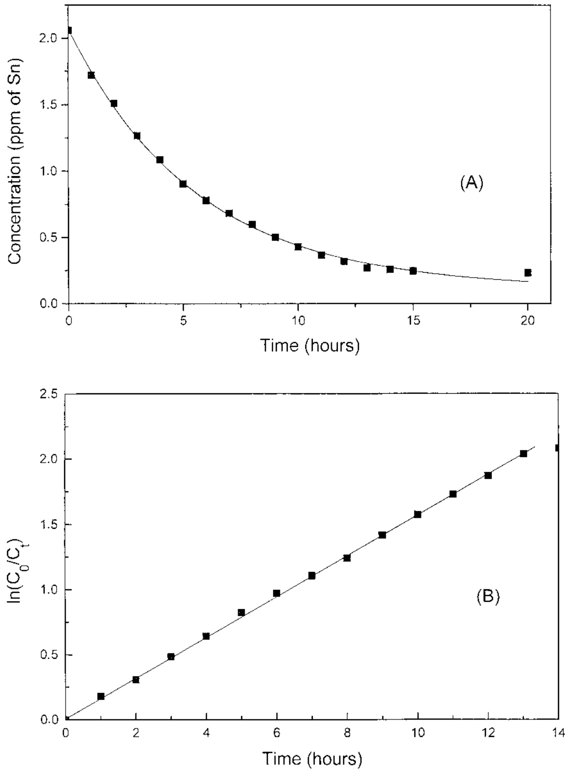
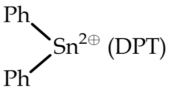
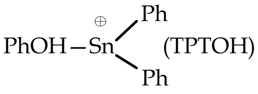
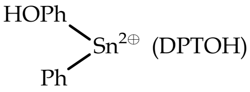


Figure 3. (A) Decrease in TPT concentration upon irradiation at 365 nm: $[Fe(III)] = 3 \times 10^{-4}$ mol L^{-1} (with 80% of monomeric species); [TPT] = 2 ppm. (B) First-order kinetics of TPT disappearance (correlation coefficient >0.99).

Table 1. Photoproducts identified and the maximum relative intensities

Photoproducts identified	Relative height of the GC peak
 $\mathrm{Ph_2Sn^{2\oplus}}$ (DPT)	100
$\mathrm{Ph{-}Sn^{3\oplus}}$ (MPT)	90
 $\mathrm{PhOH{-}\overset{\oplus}{Sn}Ph_2}$ (TPTOH)	1
 $\mathrm{(HOPh)(Ph)Sn^{2\oplus}}$ (DPTOH)	2
$\mathrm{HOPh{-}Sn^{3\oplus}}$ (MPTOH)	2
PhOH (Phenol)	3
Inorganic tin	3

with DPT and MPT. We were not able to detect any dihydroxylation of the aromatic ring. This is in agreement with a very efficient subsequent degradation of such compound by hydroxyl radicals.

Irradiation under solar light and projection to environment

A mixture of TPT (2 ppm) and iron(III) [3×10^{-4} mol l^{-1}, with near 100% of monomeric $Fe(OH)^{2+}$] was exposed to solar light and at 365 nm. We compared the rates of TPT disappearance for both systems of irradiation. After 1 h of irradiation the disappearance of 90% of the starting TPT concentration was obtained under sunlight irradiation, whereas only 40% was degraded in the same period of time in a photoreactor at 365 nm. The rate of degradation was multiplied by two under sunlight. This result shows the important part played by shorter wavelengths in the photochemical process, solar emission starting at 295–300 nm.

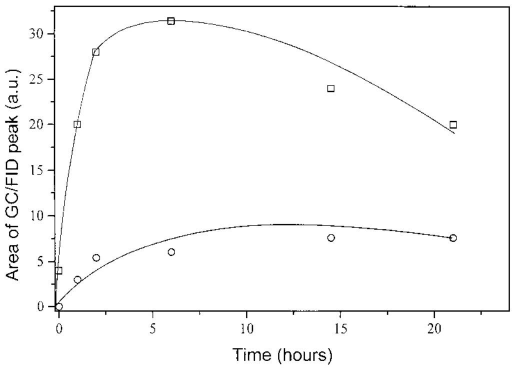


Figure 4. Evolution of DPT and MPT concentrations as a function of irradiation time at 365 nm: [Fe(III)] = 3×10^{-4} mol l^{-1} (with 80% of monomeric species); [TPT] = 2 ppm. □, DPT; ○, MPT.

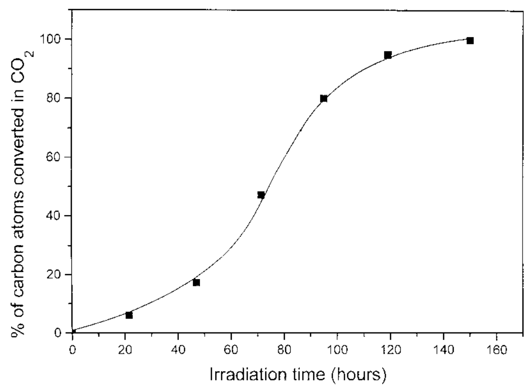


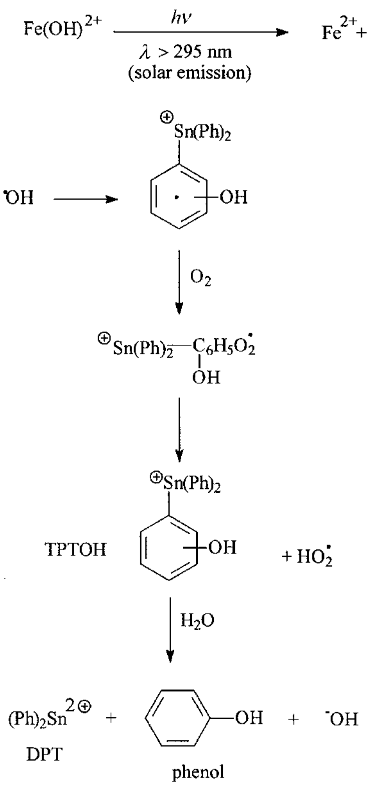
Figure 5. CO_2 formation upon irradiation at 365 nm of a mixture TPT–Fe(III): [Fe(III)] = 6×10^{-4} mol l^{-1} and [TPT] = 6 ppm.

We also compared the degradation of a solution of TPT (2 ppm) in the absence of iron(III) under sunlight irradiation. Only 30% of TPT was degraded after 9 days of irradiation instead of 90% in 1 h. The efficiency of the TPT degradation under sunlight is increased by two or three orders of magnitude in the presence of iron(III). However, direct photolysis of TPT is not negligible, and this could be the main factor of discrepancy between the results reported in the literature.

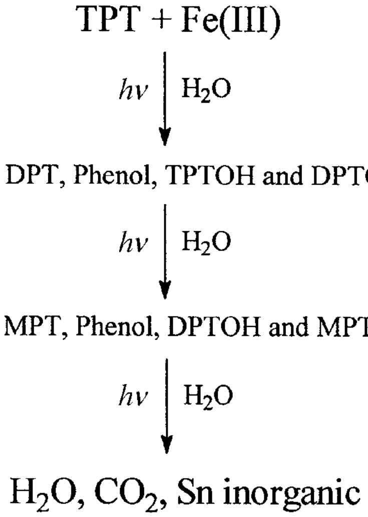
Because our starting motivation was the removal of TPT from water, we tested the efficiency of its photoinduced mineralization by iron(III). This was obtained by following CO_2 evolution during the irradiation ($\lambda_{irr} = 365$ nm) of an iron(III)/TPT solution. The concentrations used for these experiments were [Fe(III)] = 6.0×10^{-4} mol l^{-1} and [TPT] = 6 ppm. The initial monomeric species percentage was near 100%. CO_2 evolution was calculated with respect to TPT by considering that the 18 atoms of carbon would yield 18 molecules of CO_2. The formation of CO_2 is represented in Fig. 5. In the early stages of the degradation, the formation of CO_2 presents a lag period corresponding to the formation and subsequent degradation of the primary photoproducts. After 5 days of irradiation almost 100% of TPT and its photoproducts had disappeared, i.e. mineralization was achieved.

DISCUSSION

The present work illustrates the efficiency of photochemical TPT degradation, when the process is photoinduced by iron(III). As already mentioned, the first step of the process is generation of hydroxyl radicals upon irradiation of iron(III)



Scheme 1.



Scheme 2.

aquacomplexes, and more particularly $Fe(OH)^{2+}$.[14] In terms of TPT degradation the mechanism only involves an attack by hydroxyl radicals, as evidenced by the complete inhibition observed when 1% of isopropanol is added to the solution. The degradation observed in the absence of iron(III) is far less efficient than in the presence of iron(III) (approximately 700 times lower). This result shows the major impact of the presence of iron(III) on the photodegradation of TPT in aqueous solution.

The nature of the photoproducts, particularly the hydroxylated ones, shows that the major route of hydroxyl radical attack is on a phenyl group. In addition, the formation of DPT and MPT as the major photoproducts shows that the main route of degradation is a stepwise dephenylation of TPT. The overall mechanism is described in Scheme 1.

The hydroxyl radicals formed upon irradiation of $Fe(OH)^{2+}$ react on the phenyl ring of TPT and give rise to the corresponding adduct, the hydroxycyclohexadienyl radical. Similar reactions and their rate constants have been well described in the literature. The rate constants are usually very high; for instance, the k value of the reaction between hydroxyl radicals and benzene was measured by pulse radiolysis techniques and was found equal to $(7.6 \pm 1.9) \times 10^9$ mol l^{-1} s^{-1}.[17] In the presence of oxygen the adduct reacts very rapidly with oxygen to form a peroxy radical. The peroxy radical then undergoes decomposition in two principal ways: (i) reaction with itself, forming an organic peroxide; (ii) formation of a phenolic compound (TPTOH) and a hydroperoxy radical. By considering the stationary concentration of the adduct, the bimolecular reaction is more disfavoured and the monomolecular dissociation reaction is more likely. Actually, this is confirmed by the formation of the monohydroxylated compounds (TPTOH, DPTOH and MPTOH) for each organotin species. Their very low concentrations can be assigned to low stability in the solution medium, giving rise to phenol and phenyltin derivatives by hydrolysis. Any attempt to detect the formation of more hydroxylated compounds, hydroxylated either on the same phenyl ring or one hydroxy group on each phenyl group, failed, but we cannot rule out the formation of such compounds.

The set of reactions can be repeated with DPT and MPT, leading to complete dephenylation of the starting compound and the final formation of inorganic tin. A similar behaviour, a stepwise debutylation process, was observed when dealing with tributyltin.

For long irradiation times we obtained the total disappearance of TPT and of the photoproducts; all the atoms of carbon present in the triphenyltin were converted into CO_2. Complete mineralization was thus obtained (Scheme 2).

The chain of reactions in Scheme 2 leads to a step-by-step reduction of the toxicity until the formation of inorganic tin and CO_2, compounds that are innocuous for the environment. This work provides evidence for the efficiency of TPT removal from wastewater by a photoprocess with iron(III) using either artificial or solar light.

Acknowledgements

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