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Direct Detection of the Triphenylpyrylium-Derived Short-Lived Intermediates in the Photocatalyzed Degradation of Acetaminophen, Acetamiprid, Caffeine and Carbamazepine

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Abstract

Advanced oxidation processes are useful methodologies to accomplish abatement of contaminants; however, elucidation of the reaction mechanisms is hampered by the difficult detection of the short-lived primary key species involved in the photocatalytic processes. Nevertheless, herein the combined use of an organic photocatalyst such as triphenylpyrylium (TPP^+) and photophysical techniques based on emission and absorption spectroscopy allowed monitoring the photocatalyst-derived short-lived intermediates. This methodology has been applied to the photocatalyzed degradation of different pollutants, such as acetaminophen, acetamiprid, caffeine and carbamazepine. First, photocatalytic degradation of a mixture of the pollutants showed that acetaminophen was the most easily photodegraded, followed by carbamazepine and caffeine, being the abatement of acetamiprid almost negligible. This process was accompanied by mineralization, as demonstrated by trapping of carbon dioxide using barium hydroxide. Then, emission spectroscopy measurements (steady-state and time-resolved fluorescence) allowed demonstrating quenching of the singlet excited state of TPP^+. Laser flash photolysis experiments with absorption detection showed that oxidation of contaminants is accompanied by TPP^+ reduction, with formation of a pyranyl radical ($TPP^\bullet$), that constituted a fingerprint of the redox nature of the occurring process. The relative amounts of $TPP^\bullet$ detected was also correlated with the efficiency of the photodegradation process.

Keywords

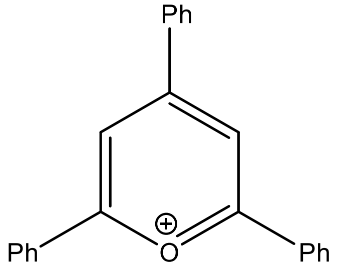
Electron transfer; laser flash photolysis; singlet excited state; time-resolved fluorescence; triplet excited state

1. Introduction

Decontamination of wastewaters derived from the industrial activities is currently a subject of active research to address the current demand of good quality water availability by the increasing population [1-3]. Advanced oxidation processes (AOPs) have demonstrated to be useful methodologies to accomplish abatement of a variety of contaminants, such as pesticides, drugs or emerging pollutants in wastewaters effluents [4, 5]. Among them, solar-driven ones are particularly interesting since they could be considered as green methodologies [1]; however, elucidation of the reaction mechanisms is hampered by the difficult detection of the short-lived primary key species involved in the photocatalytic processes [6].

In this sense, the use of organic photocatalysis as appropriate advanced oxidation process to oxidize contaminants has been widely reported [7]. Among other advantages, organic photocatalysts exhibit absorption bands in the UV-visible region that can be excited to generate transient species able to interact with the pollutants [8, 9]. Rather than to be applied for real wastewater treatments, photophysical techniques based on emission and UV-visible absorption spectroscopy have proven to be useful to gain insight into the mechanistic aspects of the photo-oxidation reactions, providing time-resolved data in the nano or microsecond scale, as they allow direct monitoring and quantification of reactive species [7].

In this context, 2,4,6-triphenylpyrylium (TPP^+) (see Fig. 1 top) is able to absorb UV-visible light (Fig. 1 bottom), and has achieved photooxidation of pesticides under real solar irradiation, through a mechanism which involves electron transfer from the pollutants [9, 10]. In fact, it has proven to oxidize pollutants from its singlet and triplet excited states and from a ground-state complex [11-14]. Nonetheless, *ca*. 50% of the molecules in their singlet excited state are able to cross to the triplet (Fig. 1 top) [11]. The triplet excited state of TPP^+ shows a characteristic transient absorption spectrum in the visible with a broad band between 450 and 600 nm; the corresponding reduced species (pyranyl radical, $TPP^{\bullet}$) resulting from a photooxidation process, through an e^- transfer mechanism, also shows a broad characteristic absorption in the visible from 450 to 600 nm, with a maximum at 550 nm (Fig. 1 bottom). Therefore, the use of TPP^+ as photocatalyst to provide direct evidence for the e^- transfer mechanism in the abatement of pollutants offers a significant advantage to the use of other photocatalysts. In fact, not only the excited states but also the reduced species are well characterized in the literature [7]. Although there is some overlap between the pyranyl radical and the triplet excited state, a biexponential analysis based on the different lifetimes and molar absorption coefficients of the two species (specifically at 550 nm), allows quantification of the reduced $TPP^{\bullet}$; this acts as a proof of the e^- transfer nature of the process, and could also be correlated to the extent of the photodegradation.



2,4,6-Triphenylpyrylium
(**TPP$^+$**)

Meaningful Photophysical Data
$\Phi_F = 0.47$
$\Phi_{ISC} = 0.53$
$\tau_S = 4 \times 10^{-9}$ s
$\tau_T = 6 \times 10^{-6}$ s
$E_S = 66$ kcal mol^{-1}
$E_T = 53$ kcal mol^{-1}

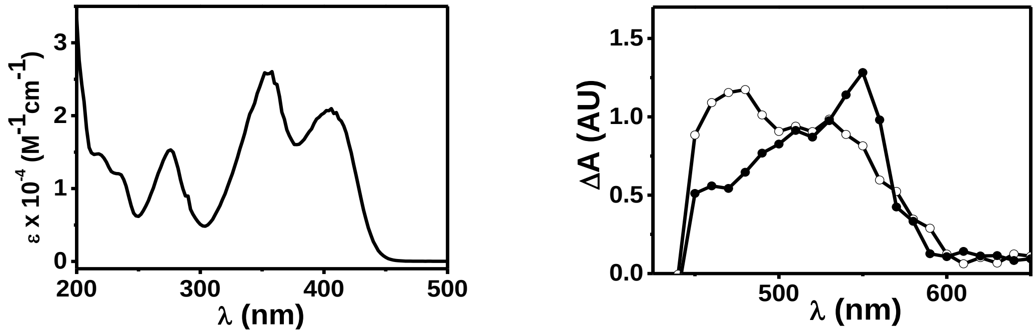
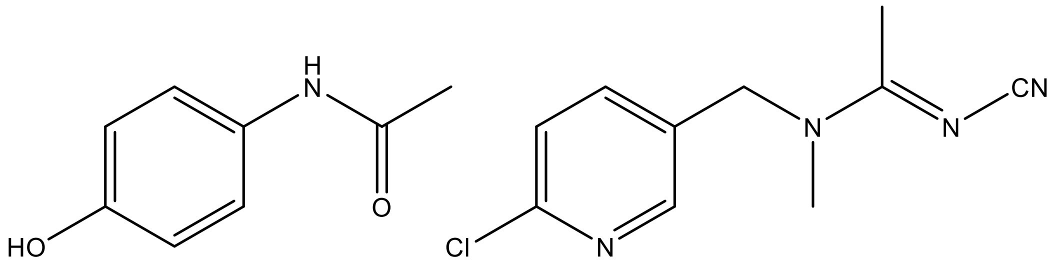


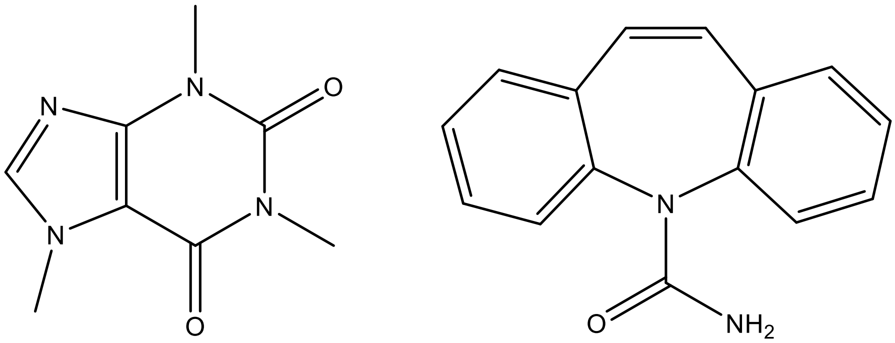
Figure 1

With this background, the aim of this work is to provide a direct and quantitative piece of evidence of the photooxidation of a variety of contaminants, and to correlate the concentration of the primary reduced species with the e$^-$ transfer mechanism. For this purpose, acetaminophen (ACF), acetamiprid (ACP), caffeine (CAF) and carbamazepine (CBZ) have been selected as representative pollutants with a variety of chemical structures that contain (hetero)aromatic rings with different capability to act as electron donors (Fig. 2). They belong to the family of emerging pollutants, which include drugs, toiletries and other chemicals of daily use, and are of increasing environmental concern [15, 16]. First, steady-state photolysis has been carried out under simulated solar irradiation in the presence of TPP$^+$, and then photophysical measurements based on emission spectroscopy (steady-state and time-resolved fluorescence) and photophysical measurements based on absorption spectroscopy (laser flash photolysis) have provided fast kinetic data. As a result, the appearance of the common key species, the reduced TPP$^{\bullet}$, has been correlated to the photooxidation process.



Acetaminophen (**ACF**)

Acetamiprid (**ACP**)



Caffeine (**CAF**)

Carbamazepine (**CBZ**)

Figure 2

2. Experimental

2.1. Reagents

Acetaminophen, acetamiprid, caffeine, carbamazepine, TPP$^+$ used as hydrogensulfate or tetrafluoroborate salt, and barium hydroxide octahydrate were purchased from Sigma Aldrich. Water used in photochemical experiments was Milli-Q grade, and HPLC quality acetonitrile, employed as solvent in photophysical measurements, was from Merck.

2.2. Solar simulated photochemical reactions

An aqueous solution (250 mL) containing the mixture of the four pollutants (at the initial concentration of 5 mg/L each) and the photocatalyst (TPP$^+$ at 10 mg/L) was introduced in an open Pyrex glass vessel; the pH was adjusted to 3 by dropwise addition of sulfuric acid, to increase stability of the photocatalyst, and then it was irradiated by means of a solar simulator (Oriel Instruments, Model 81160) equipped with a 300W Xenon lamp, which closely reproduces the solar spectrum. The reaction mixture was magnetically stirred all along the reaction time, and water was periodically added to compensate for the evaporation loss.

Aliquots were taken from the reaction mixture, filtered using 0.45 μm polypropylene and injected into a liquid chromatograph (Perkin Elmer model Flexar UPLC FX-10) equipped with a UV-Vis detector. A Brownlee analytical column (DB-C18) was used as stationary phase, and a gradient mixture of acetonitrile and 0.1% formic acid in aqueous solution was used as the eluent at a flow rate of 0.3 mL/min. The mineralization was estimated upon trapping the formed carbon dioxide as $BaCO_3$. For that purpose, an aqueous solution (80 mL) of acetaminophen (1.0 g) and TPP^+ (2.5 mg) was irradiated up to 24 hours (using the solar simulator with stirring) with a continuous flow of oxygen. The evolved CO_2 was *in situ* trapped by bubbling it through a saturated solution of $Ba(OH)_2$. The as formed precipitate was submitted to elemental analysis using a EuroEA Elemental Analyser from EuroVector Instruments and Software.

2.3. Photophysical instrumentation

Absorption spectra (UV/Vis) were performed on a Shimadzu UV-2101PC spectrometer. Steady-state fluorescence and time-resolved fluorescence experiments were performed in a FS900 fluorometer and a FL900 setup, respectively (Edinburgh Instruments). Lifetime measurements were based on single-photon-counting using a 1.5 ns pulse width hydrogen flash-lamp as excitation source. The kinetic traces were fitted by monoexponential decay functions using a deconvolution procedure to separate them from the lamp pulse profile.

Laser flash photolysis (LFP) experiments were carried out with a pulsed Nd: YAG SL404G-10 Spectron Laser Systems at the excitation wavelength of 355 nm. The energy of the single pulses (~10 ns duration) was lower than 15 mJ pulse^{-1}. The laser flash photolysis system consisted of the pulsed laser, a pulsed Lo255 Oriel Xenon lamp, a 77200 Oriel monochromator, an Oriel photomultiplier tube (PMT) housing, a 70705 PMT power supply and a TDS-640A Tektronix oscilloscope.

2.4. Photophysical experiments

Photophysical experiments were carried out in deaerated acetonitrile to increase the dynamic range and reach higher concentration of the pollutants, in quartz cells of 1 cm optical path length at room temperature.

Solutions of TPP^+ with absorbance at the excitation wavelength (405 nm) lower than 0.1 were prepared for the steady-state and time-resolved fluorescence experiments. The quenching experiments were performed upon adding concentrations of pollutants in the range $0 – 7 \times 10^{-3}$ M.

For the laser flash photolysis experiments, solutions of TPP^+ at 7×10^{-5} M were employed, and increasing amounts of pollutant ($0 - 7 \times 10^{-5}$ M) were added to them.

3. Results and discussion

3.1 Solar simulated photodegradation of the pollutants

An aqueous solution containing the four selected pollutants and TPP^+ was acidified, to guarantee the stability of the photocatalyst under the experimental conditions [17], and then irradiated with a solar simulator [18]. Fig. 3A shows the evolution of the relative concentration of each pollutant *vs.* irradiation time. As anticipated from the different electron-donating ability of the pollutants, the photodegradation rates showed marked variations in the series. Thus, ACF showed the highest photodegradation rate, while CBZ and CAF were much more reluctant, and removal of ACP was negligible under the employed experimental conditions. More specifically, more than 99.5 % of ACF was removed after 90 min of irradiation in the presence of TPP^+, while only *ca.* 20% of CAF and CBZ were removed after 180 min (percentages based on the quantification limits of the chromatographic analysis). In all cases, control experiments in darkness (Fig. 3B) or in the absence of TPP^+ (Fig. 3C) showed no reaction or marginal direct photolysis, respectively.

The photodegradation of ACF was further investigated upon monitoring the formation of CO_2 (see Fig. 3D). For this purpose, a new batch containing ACF and TPP^+ was irradiated with continuous flow of oxygen. The CO_2 obtained upon mineralization was bubbled through a saturated aqueous solution of $Ba(OH)_2$, in which it was converted into $BaCO_3$ that precipitated at the bottom. After 24 hours irradiation the precipitate was filtered and analyzed. Elemental analysis of the precipitate (C: 7.049 %) after photodegradation unequivocally demonstrated the formation of $BaCO_3$.

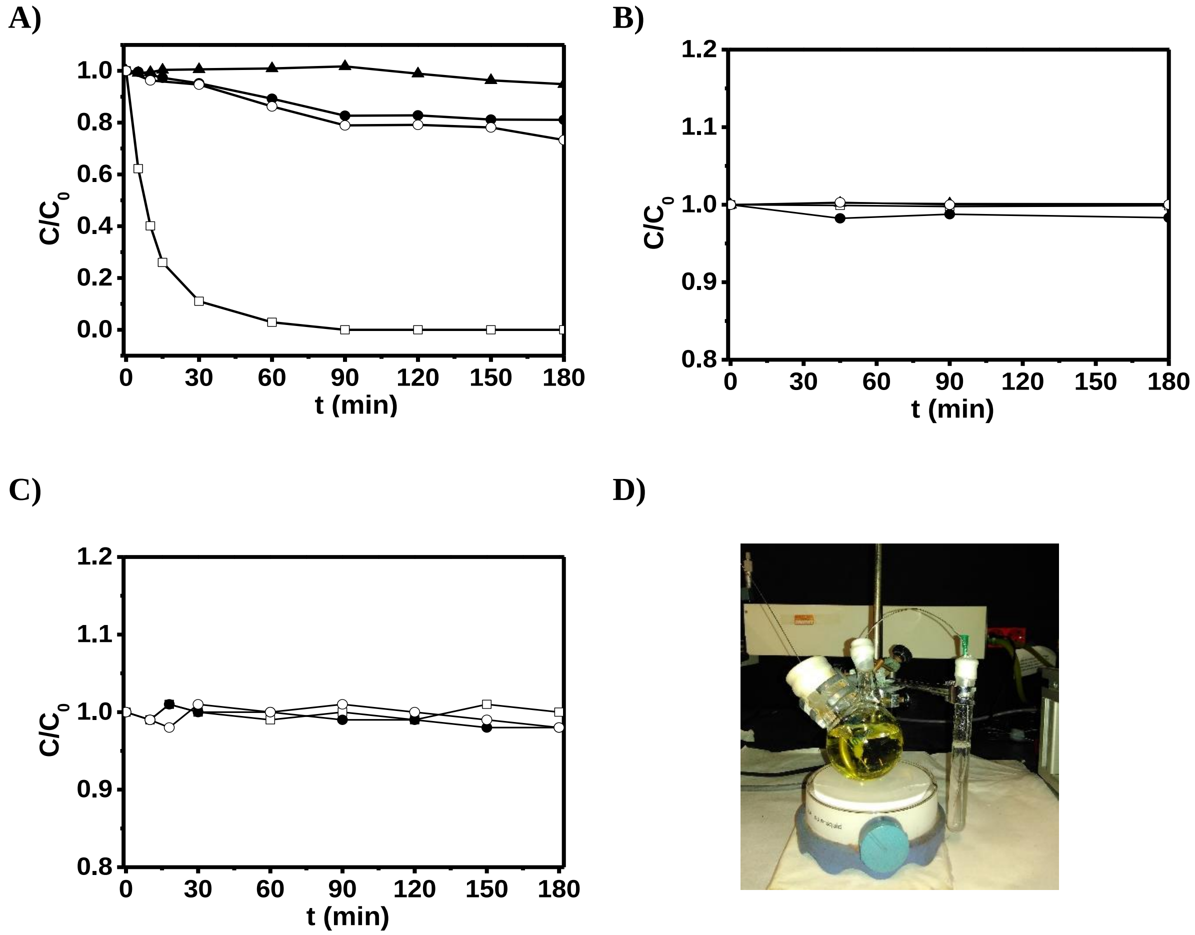


Figure 3

3.2. Photophysical studies

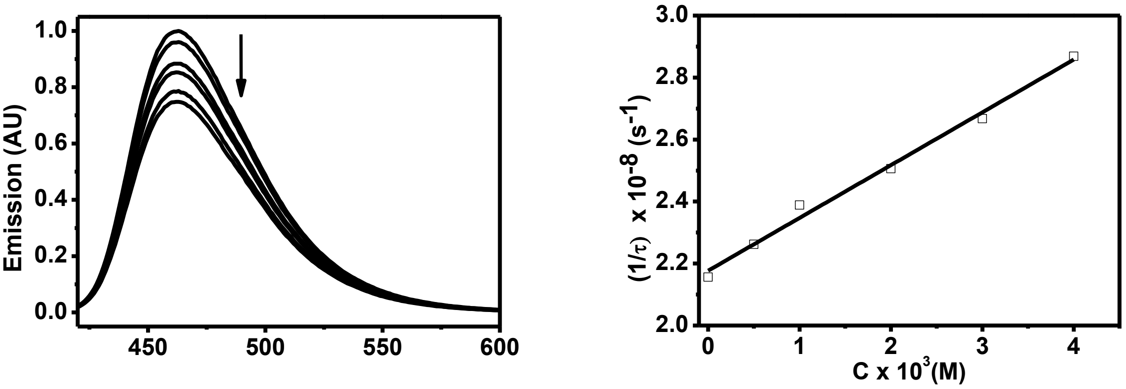
Redox potentials of TPP^+ are 2.5 V and 2.0 V *vs* SCE, from its singlet and triplet excited states, respectively, which means that this photocatalyst is a strong oxidant from either excited state [9]. Hence, photophysical studies including steady-state and time resolved fluorescence and laser flash photolysis were undertaken for each contaminant. Dynamic quenching of the singlet excited state would indicate that the e^- transfer is feasible from this excited state. In addition, laser flash photolysis would show the typical absorption band characteristic of the reduced species, if an e^- transfer process is taking place.

3.2.1. Emission spectroscopy: fluorescence quenching studies

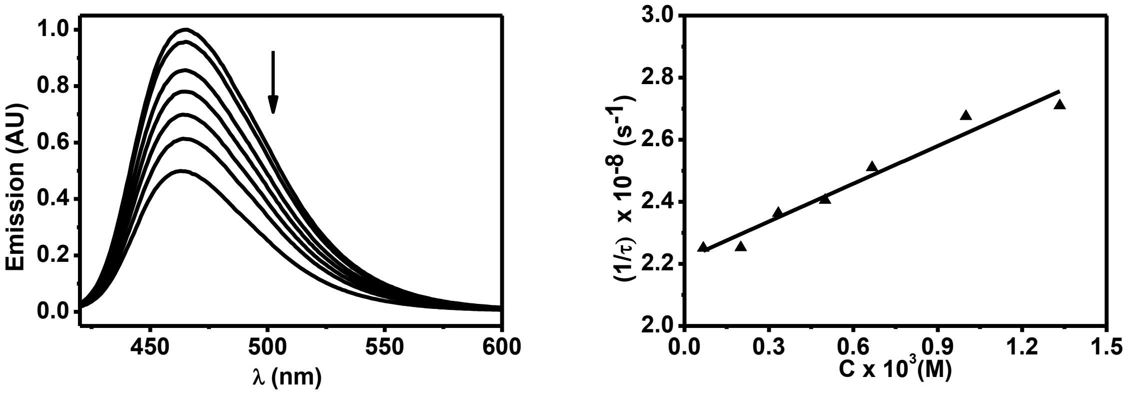
Steady-state and time-resolved experiments were performed in deaerated acetonitrile to investigate the potential participation of the singlet excited state of TPP^+ in the photodegradation of the contaminants (Fig. 4). In all cases a decrease in the typical emission and also in the singlet lifetime of $^1(TPP^+)^*$ was observed upon addition of the contaminants. The corresponding quenching rate constants were determined applying the Stern-Volmer relationship, between I_o/I or τ_o/τ and pollutant concentration. Specifically, k_{qS} values were 1.8 x 10^{10}; 3.6 x 10^{10}; 1.4 x 10^{10} and 1.5 x 10^{10} $M^{-1}s^{-1}$, for ACF, ACP, CAF and CBZ, respectively. The obtained values confirmed the dynamic involvement of the singlet excited state in all cases, with values in the range of the diffusion limit (k_{diff} = 1.9 x 10^{10} $M^{-1}s^{-1}$ in CH_3CN) [19].

Singlet excited states have short lifetimes (in the order of nanoseconds) compared to the relatively long lifetime of triplet excited states (in the range of microseconds), and therefore their participation in the photodegration is more unlikely. However, steady-state and time-resolved fluorescence spectroscopy experiments are required to support or discard this participation [7, 20, 21]. In fact in this particular case quenching of the singlet excited state of $^1(TPP^+)^*$ by the four contaminants has proven to be very efficient.

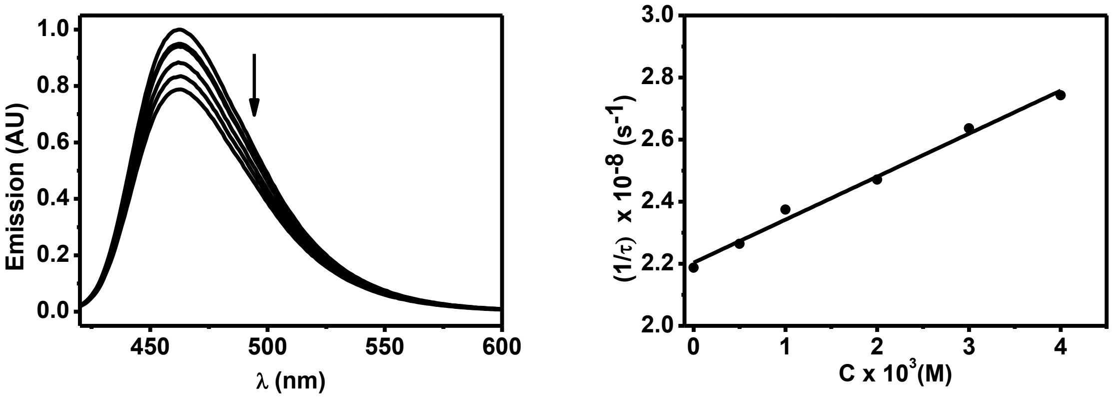
A)


Emission (AU)
1.0
0.8
0.6
0.4
0.2
0.0
450
500
550
600
$(1/\tau)\ \times 10^{-8}\ (s^{-1})$
3.0
2.8
2.6
2.4
2.2
2.0
0
1
2
3
4
C x 10^3(M)

B)


Emission (AU)
1.0
0.8
0.6
0.4
0.2
0.0
450
500
550
600
λ (nm)
$(1/\tau)\ \times 10^{-8}\ (s^{-1})$
3.0
2.8
2.6
2.4
2.2
2.0
0.0
0.3
0.6
0.9
1.2
1.5
C x 10^3(M)

C)


Emission (AU)
1.0
0.8
0.6
0.4
0.2
0.0
450
500
550
600
λ (nm)
$(1/\tau)\ \times 10^{-8}\ (s^{-1})$
3.0
2.8
2.6
2.4
2.2
2.0
0
1
2
3
4
C x 10^3(M)

D)

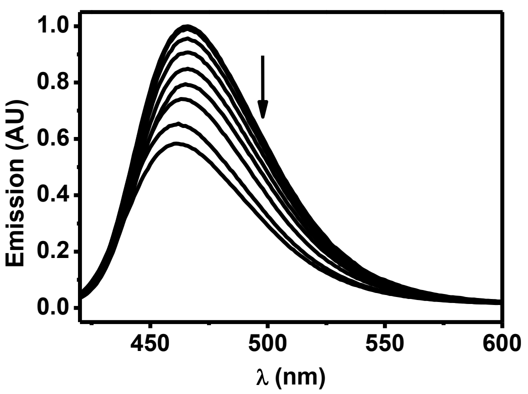
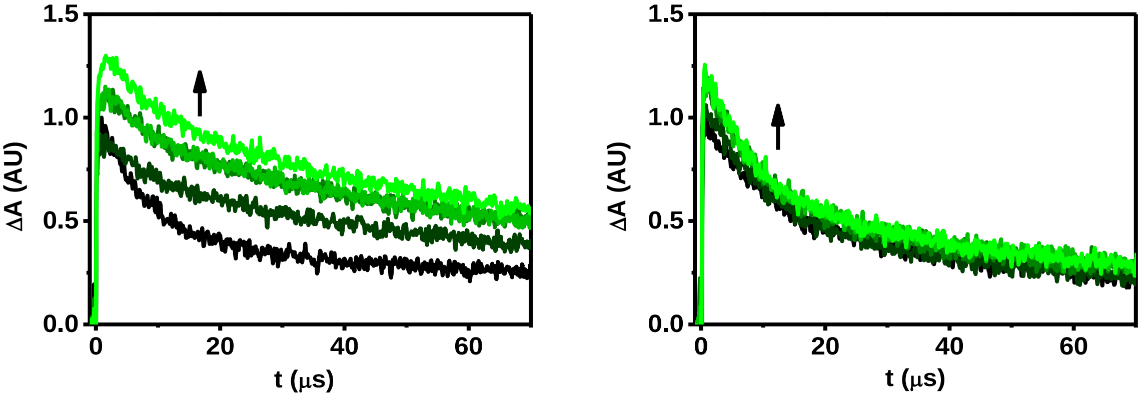


Figure 4

3.2.2. Transient UV-visible absorption spectroscopy

Laser flash photolysis (LFP) experiments upon excitation of TPP^+ at 355 nm were performed in the presence of increasing concentrations of the pollutants. The obtained traces, recorded at 550 nm, where the triplet excited state and the reduced species of the photocatalyst absorb, are shown in Fig. 5.

A) **B)**



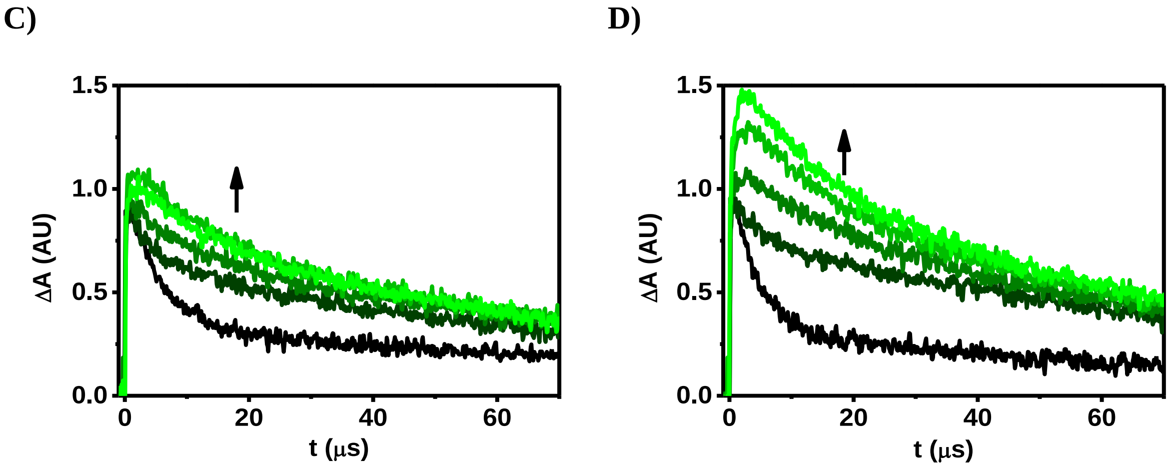


Figure 5

Quenching of singlet excited state does not involve necessarily an electron transfer process, since also formation of a complex between the photocatalyst and the contaminant can be responsible for such a quenching [14]. Therefore, to support the photoredox process, detection of the at least one of the species resulting from the electron transfer is desirable [18]. In this case, the key piece of evidence supporting the e$^-$ transfer mechanism comes from the analysis of the intensity of the traces shown in Fig. 5. First, the absorption recorded at 550 nm in the absence of contaminants is due to the characteristic absorption of the triplet excited state of TPP, ^{3}(TPP$^+$)* (initial trace in the four cases, in black). Nevertheless, the observed increase in this absorption upon addition of increasing concentration of the pollutants can only be due to the contribution of a species different from the triplet and absorbing at the same wavelength with a higher molar absorption coefficient, such as the reduced pyranyl radical, TPP$^\bullet$ (see Fig. 5 and also Fig. 1 bottom). The appearance of the pyranyl radical within the laser pulse (at the initial recording time) is in agreement with quenching of the singlet excited state shown in all cases (see previous section) due to an electron transfer mechanism.

Accordingly, the new traces needed a biexponential analysis to get a good fitting, which act as an additional piece of evidence supporting the redox process. For that purpose, a typical biexponential analysis based on the different lifetimes of the two species (τ_T *ca.* 5-8 μs *vs* τ_{rad}

ca. 34-36 μs) was applied [9]. As a result, the obtained pre-exponential factors allowed quantifying the concentration of both species, as shown on Fig. 6A for the pyranyl radical and Fig. 6B for the triplet.

From these results we can conclude that the appearance of the reduced TPP$^{\bullet}$, which is a requirement of the photooxidation process, acts as a proof of the first step, since the corresponding pollutant radical cations are not revealed in the available UV-visible spectral window (300-700 nm). Accordingly, the lack of photodegradation of ACP is in agreement with the very low concentration of the pyranyl radical observed in this case.

Therefore, the postulated mechanism for the photooxidation of the pollutants is shown in Scheme 1. The electron transfer mechanism as the initial step from the excited states of the photocatalyst has been demonstrated upon detection and quantification of the primary reduced pyranyl radical species. Once the e$^-$ transfer has occurred, subsequent chain reactions starting from the photooxidized radical cation can take place, giving rise to a different extent of the overall photodegradation process. In particular, the fact that the ACF was completely removed after only 90 min of irradiation, much faster than the rest of pollutants, could be explained by alternative and more efficient reaction pathways happening from the resulting phenoxyl radical.

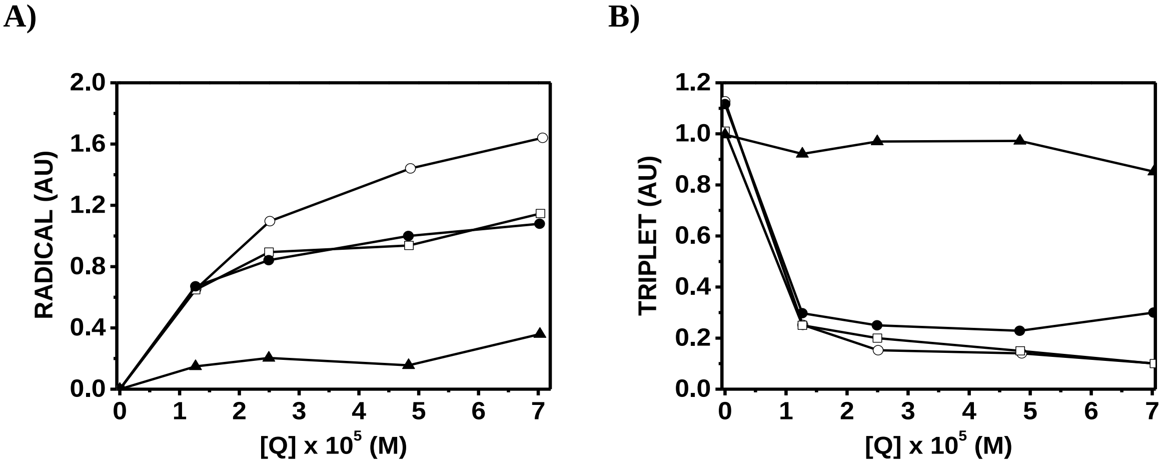
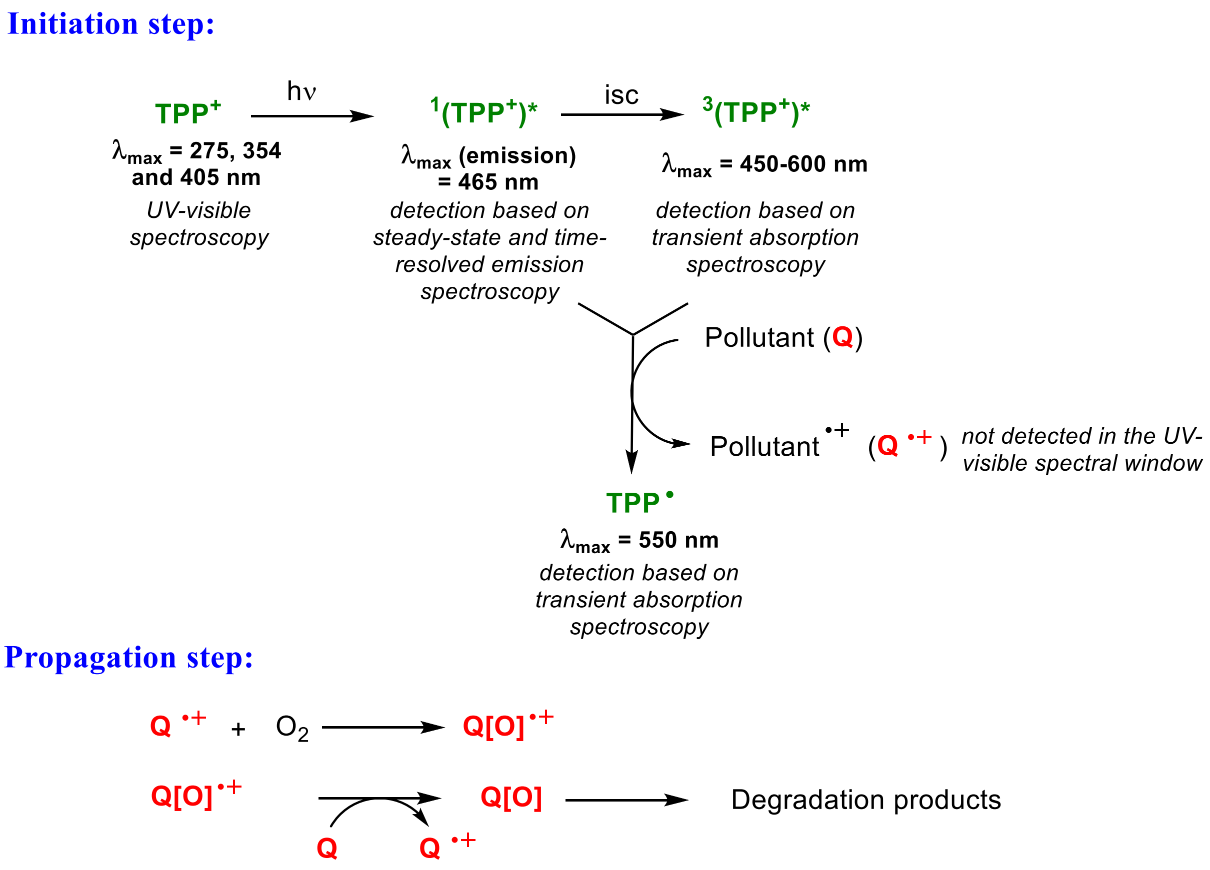


Figure 6



Scheme 1

Conclusions

The triphenylpyrylium (TPP$^+$) photocatalyzed oxidation of acetaminophen, acetamiprid, caffeine and carbamazepine can be appropriately monitored by direct detection of all the short-lived intermediates derived from the photocatalyst. Thus, fluorescence measurements (steady-state and time-resolved) allow characterizing the TPP$^+$ singlet excited state through its spectrum and lifetime; whereas laser flash photolysis provides parallel information on the triplet excited state. Oxidation of the contaminants is accompanied by TPP$^+$ reduction, with formation of a pyranyl radical (TPP$^•$). This reduced species can be directly detected by laser flash photolysis, which constitutes a fingerprint of the redox nature of the photodegradation process. The relative amounts of $TPP^{\bullet}$ detected upon addition of the contaminants can be correlated with the efficiency of the photodegradation process.

Acknowledgements

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Figure captions

Figure 1. Top: chemical structure of 2,4,6-triphenylpyrylium (TPP^+) together with some meaningful photophysical data; bottom left: TPP^+ UV-visible absorption spectrum and bottom right: transient absorption spectra corresponding to $^3(TPP^+)^*$ (○) and $TPP^\bullet$ (●).

Figure 2. Chemical structures of the selected contaminants.

Figure 3. A) Plot of the relative concentration of ACF (□), ACP (▲), CAF (●) and CBZ (○) at C_o= 5 mg L^{-1} and pH = 3, *vs*. solar simulated irradiation time, in the presence of 10 mg L^{-1} of TPP^+; **B)** Control experiment: relative concentration of ACF (□), ACP (▲), CAF (●) and CBZ (○) at C_o= 5 mg L^{-1} and pH = 3, *vs*. time, in the presence of 10 mg L^{-1} of TPP^+ in darkness; **C)** Control experiment: direct photolysis of ACF (□), CAF (●) and CBZ (○) at C_o= 5 mg L^{-1} and pH = 3, *vs*. solar simulated irradiation time, in the absence of TPP^+; **D)** Image showing the photoirradiation of ACF in the presence of TPP^+ with continuous flow of oxygen. The system is connected to a saturated aqueous solution of $Ba(OH)_2$ to trap the obtained CO_2.

Figure 4. Steady-state $^1(TPP^+)^*$ fluorescence quenching (λ_{exc} = 405 nm, left column) and Stern-Volmer plots, obtained from the time-resolved experiments (right column), upon increasing concentration of contaminants in deaerated CH_3CN: ACF (A), ACP (B), CAF (C) and CBZ (D).

Figure 5. Kinetic traces recorded at 550 nm, obtained upon LFP excitation (λ_{exc} = 355 nm) of deaerated acetonitrile solutions of TPP^+ (7 x 10^{-5} M) upon increasing pollutant concentrations (0 – 7 x 10^{-5} M): ACF (A), ACP (B), CAF (C) and CBZ (D).

Figure 6. Evolution of the concentration of pyranyl radical (**A**) and triplet excited state (**B**) upon increasing amounts of ACF (□), ACP (▲), CAF (●) and CBZ (○).

Scheme 1. Electron transfer mechanism in the photodegradation of the pollutants in the presence of TPP^+, happening from either the singlet or the triplet excited state. The primary reduced pyranyl radical and oxidyzed pollutant radical cation are indicated. The detection technique applied for each species is specified.

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