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Pyrylium salt-photosensitized degradation of phenolic contaminants present in olive oil wastewater with solar light Part III. Tyrosol and *p*-hydroxyphenylacetic acid

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Abstract

Photodegradation of tyrosol and *p*-hydroxyphenylacetic acid, present in olive oil wastewater, can be achieved using 2,4,6-triphenylpyrylium salt as solar photocatalyst. Fluorescence quenching measurements support the involvement of electron transfer as the key step in this process, with formation of substrate-derived radical cations. Important degradation yields are achieved. Other advanced oxidation methods (ozone and/or UV-radiation) have been tested as well; as expected, tyrosol and *p*-hydroxyphenylacetic acid abatement is faster, but ozone and UV are dangerous and expensive for industrial uses. However, ozone and UV do not show an important synergistic effect in tyrosol and *p*-hydroxyphenylacetic acid oxidation. *p*-Hydroxymandelic acid and *p*-hydroxybenzaldehyde have been detected and identified by HPLC as intermediates; on the basis of these data, a reaction mechanism involving oxidation at the benzylic position is proposed. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Phenolic compounds present in olive oil mill wastewater constitute an important environmental problem in the Mediterranean countries [1]. Due to their toxicity and reluctance towards biological degradation [2], alternative methods are required to achieve the abatement of phenols prior to any biological treatment [3,4].

Advanced oxidation methods could provide a solution for such environmental problem [5–14]. They involve highly oxidizing species like ozone or hydroxyl radical and produce a strong oxidation of the target pollutants, often leading to complete mineralization. Unfortunately, this type of treatment makes use of aggressive oxidants, which can be expensive or even dangerous.

An oxidation method that avoids the use of strong oxidizing agents is solar photocatalysis [15,16]. In this context, pyrylium salts are known to be good

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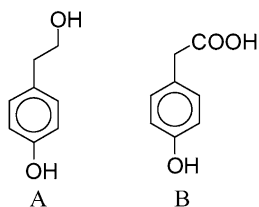
Scheme 1. Structures of tyrosol (A) and *p*-hydroxyphenylacetic acid (B).

photocatalysts acting via an electron-transfer mechanism [17]. The 2,4,6-triphenyl substituted derivative is able to work under solar irradiation: it has two intense absorption bands with maxima at 350 and 400 nm with the tail of the long wavelength band extending into the 450 nm region. When excited, the 2,4,6-triphenylpyrylium cation becomes a strong oxidizing agent, capable to withdraw an electron from the pollutant.

In previous papers [18–20], we have dealt with the solar photodegradation of phenolic pollutants present in the olive oil mill wastewater, catalyzed by a pyrylium salt. After checking the feasibility of the approach with *p*-coumaric acid as model compound, the study was extended to the families of cinnamic acid and benzoic acid derivatives. In the present communication, we wish to report on the analogous treatment of the third (and last) major type of phenolic contaminants present in those wastewater: *p*-hydroxyphenylacetic acid and *p*-hydroxyphenylethanol (tyrosol) (Scheme 1). The results will be compared with those obtained by ozone treatment of the same compounds.

2. Experimental

2.1. Reagents and photocatalysts

The required substrates (*p*-hydroxyphenylacetic acid and tyrosol) were supplied by Aldrich. The photocatalyst 2,4,6-triphenylpyrylium hydrogensulfate (Aldrich) was added to the aqueous solution of the substrates without further purification. Water employed was of Milli Q grade. *p*-Hydroxymandelic acid, *p*-hydroxybenzaldehyde, *p*-hydroxybenzoic acid, protocatechuic acid, protocatechuic aldehyde,

maleic acid and oxalic acid, used as standards, were also supplied by Aldrich.

Ozone was supplied by a generator (ozogas, TRCE 4000), able to produce up to $8 \, \text{g} \, \text{h}^{-1}$ ozone, when it was fed with oxygen. In our experiments, production was fixed in $4 \, \text{g} \, \text{h}^{-1}$ ozone and the gas flow was $3 \, \text{nl} \, \text{min}^{-1}$.

2.2. Reactions and analysis

Irradiations were performed both with a solar simulator and with real sunlight. The solar simulator employed was Oriel Instruments model 68811 equipped with a polychromatic Xenon lamp (300 W) whose emission spectrum closely matches that of sunlight at the earth surface. Solar irradiations were performed in sunny days during September 2000. Some experiments were repeated in December and no significant differences were observed. Sunlight exposure always started at 10.00 h.
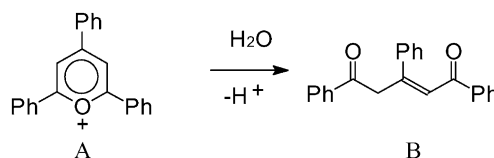
To study the stability of the pyrylium salt, aqueous solutions of this compound were prepared with an initial concentration of $10 \, \text{mg} \, \text{l}^{-1}$. The pH was adjusted with diluted solutions of HCl or NaOH. The reaction was followed by means of UV–VIS spectrophotometry, measuring at 400 nm.

The concentration of the substrate was 0.001 M for most of the photocatalytic reactions [21] and the amount of pyrylium salt was 5% (w/w) that of the substrate. The volume was 250 ml for the solar irradiation and 100 ml for the experiments with the solar simulator. The reactor consisted in an open Pyrex glass vessel. Magnetic stirring was kept along the reaction and no extra air was bubbled into the solution. To compensate for the small evaporation, some water was added periodically to keep a constant volume. Control experiments were run in the dark. Blanks experiments using no photocatalyst, but exposed to sunlight, were also performed.

In the ozonizations 250 ml of 0.005 M solutions of substrate were used. The reactions were made in a glass reactor, which has approximately 1 l capacity [22]. The reactor was submerged in a thermostatic bath and kept at the desired temperature. Periodically, samples were taken through an outlet to analyze the substrate degradation and the intermediates that are formed. Eventually, the reactor was equipped with an axial immersion lamp Heraeus TNN 15/35 (low pres-

sure mercury), which emits nearly monochromatic radiation at 254 nm.

Samples were analyzed by HPLC (Perkin Elmer Autosystem XL with a diode-array detector and a Split injector) under the conditions detailed in a previous paper [19].

2.3. Fluorescence measurements

The steady state fluorescences were obtained with a FS900 Edinburgh Analytical Instruments apparatus, equipped with a 450 W xenon lamp. The samples consisted in an acidified aqueous solution of pyrylium salt with different concentrations of substrate. These solutions were placed into quartz cells of 1 cm path length, and deoxygenation was made bubbling argon.

3. Results and discussion

3.1. Solar photodegradation catalyzed by a pyrylium salt

Aqueous 0.001 M solutions of tyrosol and p-hydroxyphenylacetic acid containing 2 mg of triphenylpyrylium hydrogensulfate (5% (w/w)) were submitted to solar exposure. The percentages of photodegradation versus time are shown in Fig. 1. In both cases the abatement achieved was very similar, 45–50% after 6 h of solar exposure.

Scheme 2. Hydrolysis of triphenylpyrylium ion.

A plot of the logarithm of the relative concentration of the substrate ($\ln(C/C_0)$) versus time shows a linear behavior during the early stages of the reaction (Fig. 1). The pseudo first order rate constants (k), calculated from the initial slopes were very similar: $4.1 \times 10^{-3}\,\mathrm{min}^{-1}$ for tyrosol and $4.4 \times 10^{-3}\,\mathrm{min}^{-1}$ for p-hydroxyphenylacetic acid.

The non-linearity observed after 2–3 h could be due to the hydrolytic opening of the pyrylium ring A to a non-active diketone B (Scheme 2). To check this hypothesis, the UV spectra of pyrylium salt under the employed conditions (pH = 3) were measured after different times of solar exposure. Indeed Fig. 2 shows that photobleaching of the pyrylium ion does actually occur.

The hydrolytic reaction follows a first order kinetics and the rate constants have been calculated at different pH, irradiating with the solar simulator (300 W). The results shown in Table 1 indicate that (a) the bleaching reaction is much faster under irradiation than in the dark and (b) the pyrylium ion is more stable under acidic conditions.
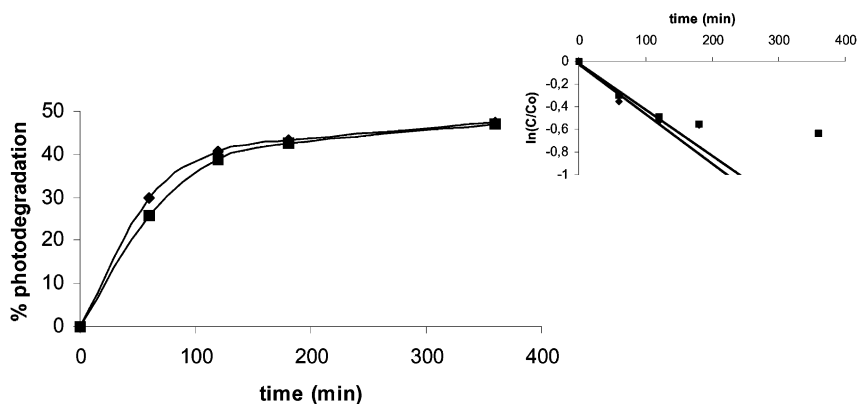
Fig. 1. Photodegradation of tyrosol (■) and p-hydroxyphenylacetic acid (◆) when submitted to solar irradiation with 5% (w/w) of pyrylium salt used as catalyst (pH = 3). Insert: first order photodegradation kinetics.
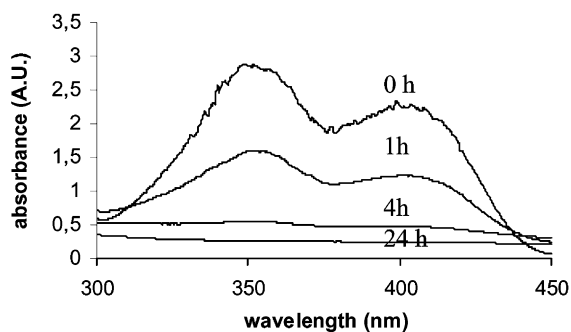
Fig. 2. Spectra of pyrylium salt in acidic media (pH = 3) when submitted to solar exposure.
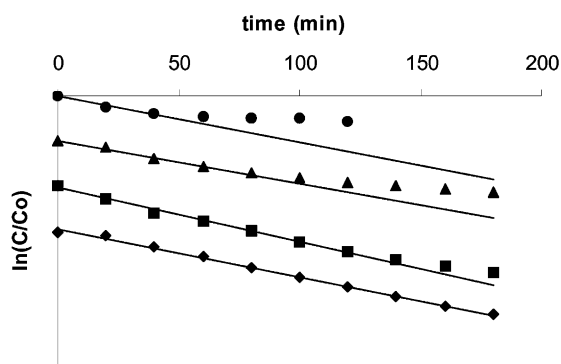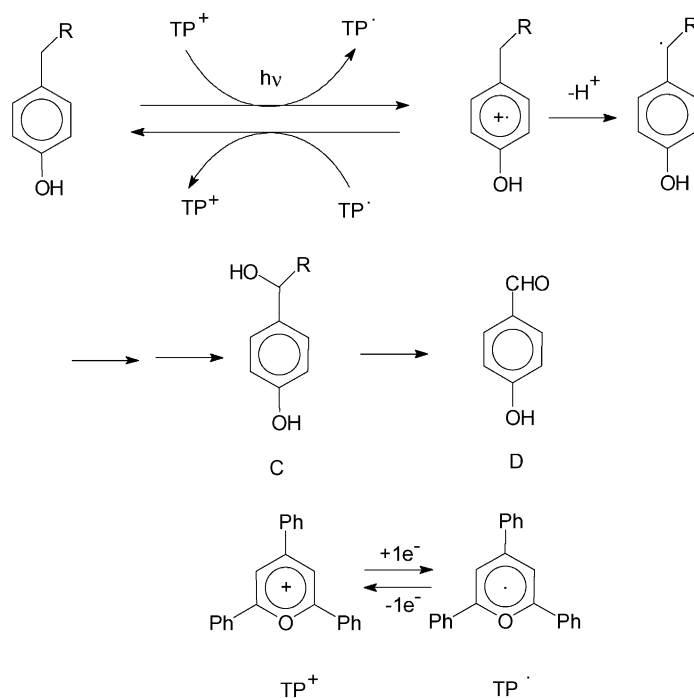

Fig. 3. *p*-Hydroxyphenylacetic acid photodegradation (solar simulator) catalyzed by pyrylium salts at different pH values. Plot of $\ln(C/C_0)$ vs. time. Lines have been displaced downwards an arbitrary value. pH values are 6.5 (●), 4.1 (▲), 3.5 (■), and 1.8 (◆).

In view of the limited stability of the pyrylium salt under non-acidic conditions, a series of experiments were performed to study the effect of pH on the rate of photodegradation. Samples were irradiated in the solar simulator and the pH was adjusted with hydrochloric acid or sodium hydroxide. The results shown in Fig. 3 confirm the expectations: in acidic medium, the pyrylium cation is stable and the same kinetic constant $(0.001\,M^{-1}\,s^{-1})$ is kept all along the reaction time. Conversely, at less acidic pH, the lack of stability of the pyrylium salt results in a clear decrease of the reaction rate in the later stages of the process. This effect is more pronounced as the pH value increases. It is interesting that the photostability of the pyrylium ion strongly increases when it is absorbed onto solid supports, hence, the use of pyrylium-based heterogeneous photocatalysts could be more convenient for practical applications [23–30].

By contrast with the two previously studied families of phenolic compounds [19,20], the photocatalyzed degradation of tyrosol and *p*-hydroxyphenylacetic acid leads to detectable amounts of some intermediates, such as *p*-hydroxymandelic acid (C) and

p-hydroxybenzaldehyde (D) (Scheme 3). This fact indicates that, besides the usual attack to the aromatic ring, there is an oxidation of the benzylic position, following the sequence shown in Scheme 3. This is supported by an independent experiment carried on with *p*-hydroxymandelic acid (250 ml, 0.001 M) which was submitted to solar exposure with 5% of pyrylium salt. The result was formation of *p*-hydroxybenzaldehyde as the only primary product.

Blank controls and dark controls were also run, and no degradation of the substrate was observed. Another experiment was performed to check the influence of changing the concentration of the catalyst, to make sure that a plateau behavior was also observed in the employed concentration range with the solar simulator. Even increasing the amount of catalyst up to 15% (w/w), no significant difference was found for the determined k values $(0.0012\,min^{-1}$ in both cases).

3.2. Photophysical studies

Further experiments were done to study the possible quenching of the singlet excited state of 2,4,6-triphenylpyrylium cation by tyrosol and *p*-hydroxyphenylacetic acid. The fluorescence emission of this cation in aqueous solution was measured using different concentrations of the substrate. It can be observed that there is a linear relationship between the relative decrease of the fluorescence emission (I/I_0) and the concentration of quencher $([Q])$ for both

Table 1
First order rate constants, *k*, for 2,4,6-triphenylpyrylium ion hydrolysis at different pH

pH	k (min^{-1}; light)	k (min^{-1}; dark)
0.9	–	–
1.8	0.0011	–
3.5	0.0046	0.0010
4.5	0.0184	0.0058

Scheme 3. Mechanistic pathways for the photodegradation of *p*-hydroxyphenylacetic acid resulting from oxidation at the benzylic position.

compounds, tyrosol and *p*-hydroxyphenylacetic acid (Fig. 4), expected for a Stern–Volmer behavior. The Stern–Volmer constants (K) were calculated from the slope of the straight line [31].

The rate constant (k_q) for the electron transfer process can be calculated by dividing K between the
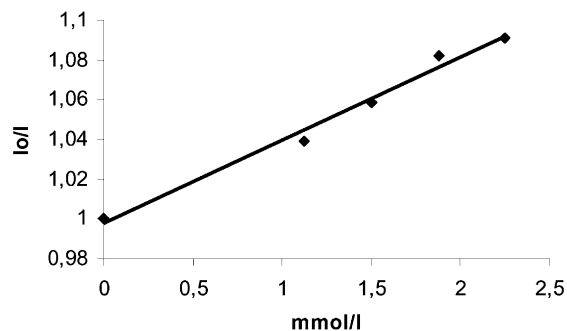

Fig. 4. Stern–Volmer relationship between the decrease in the emission of fluorescence of 2,4,6-triphenylpyrylium in the presence of different concentrations of *p*-hydroxyphenylacetic acid. A similar behavior can be observed for tyrosol.

lifetime of the singlet excited state of the pyrylium salt in aqueous solution (3.9 ns). The values obtained for tyrosol and *p*-hydroxyphenylacetic acid were very similar (ca. $1.1 \times 10^{10}\,M^{-1}\,s^{-1}$). This fact can be easily understood considering that the substitution on the aromatic ring is the same in both cases, and thus, the only difference is the substitution of a carbon atom that is quite far away from the redox active moiety. This pattern is in agreement with the results obtained in the solar reactions, where the degradation rate constants are similar for both pollutants.

This behavior is different from that previously observed for the cinnamic and benzoic acid derivatives having a *p*-hydroxy substitution ($k_q = 4.2 \times 10^{10}\,M^{-1}\,s^{-1}$ for *p*-coumaric acid and $1.5 \times 10^{10}\,M^{-1}\,s^{-1}$ for *p*-hydroxybenzoic acid) [19,20] (Fig. 5); while the quenching rate constants are lower for tyrosol and *p*-hydroxyphenylacetic acid, the degradation reactions are faster than for the other families. This can be attributed to the presence of benzylic hydrogens that could favor irreversible deprotonation of the initially formed radical cation,
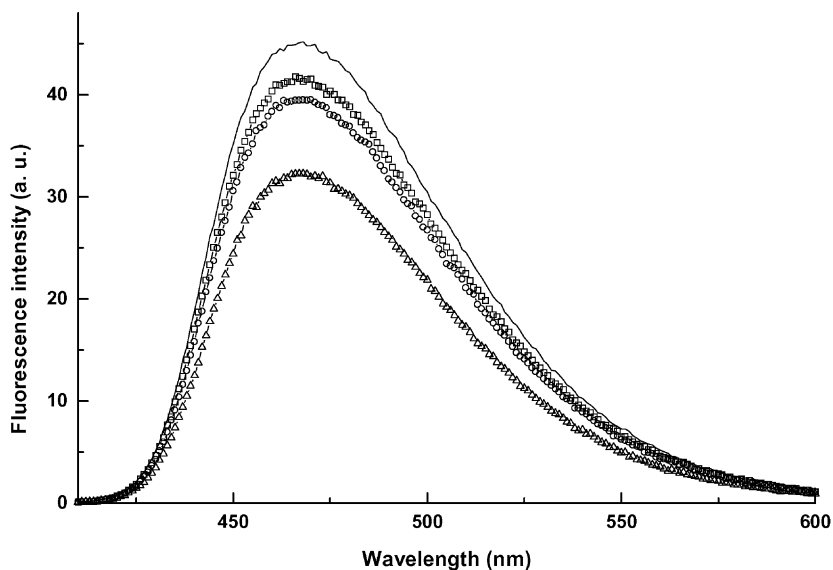
Fig. 5. Quenching of the fluorescence emission of the 2,4,6-triphenylpyrylium cation by different substrates: (□) *p*-hydroxyphenylacetic acid, (○) *p*-hydroxybenzoic acid, (△) *p*-coumaric acid. The upper continuous line is the fluorescence emission in absence of substrate.

minimizing the possible energy waste associated with back electron transfer within the primary radical ion pair.

3.3. Ozonization reactions

Tyrosol and *p*-hydroxyphenylacetic acid (250 ml of 0.005 M solutions) were ozonized in acid as well as in basic media. Parallel experiments were run in the dark and upon UV-irradiation (254 nm lamp). The disappearance of the starting compounds was studied under the above conditions; the data obtained for *p*-hydroxyphenylacetic acid are shown in Fig. 6.

In order to obtain more quantitative data on the reaction rate, the kinetic constants were calculated. Plots of the concentration of substrate versus time fitted
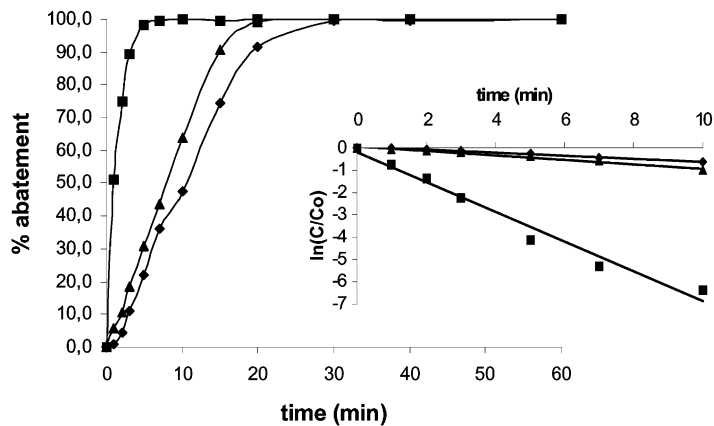

Fig. 6. Ozone abatement of *p*-hydroxyphenylacetic acid in different media: (◆) ozone in acidic media (pH = 3), (▲) ozone/UV in acidic media, (■) ozone in basic media. Insert: first order kinetics for *p*-hydroxyphenylacetic acid abatement. Plot of $\ln(C/C_0)$ vs. time.

Table 2
Pseudo first order rate constants, k (min^{-1}), obtained for degradation of p-hydroxyphenylacetic acid (A) and tyrosol (B) with ozone

	A	B
Ozone (pH = 3)	0.070	0.185
Ozone/UV (pH = 3)	0.085	0.216
Ozone (pH = 9)	0.825	1.25
Ozone/UV (pH = 9)	0.840	1.34

first order kinetics (Fig. 6). The k values are given in Table 2. Three conclusions can be obtained from these data: (a) the degradation is faster in the case of tyrosol, (b) the reaction is approximately 10 times faster in basic media and (c) UV-radiation does not accelerate significantly the ozonization reaction, thus, there is no significant synergetic effect of ozone/UV.

The intermediates formed along the reaction were carefully analyzed. In this case no intermediate reached an important concentration (higher than 10^{-5} M) with the only exception of highly oxidized compounds such as oxalic acid. Besides, trace amounts of p-hydroxymandelic acid and p-hydroxybenzaldehyde, arising from attack to the benzylic position, were detected. These results are clearly different from those obtained for p-coumaric acid, were significant amounts of various intermediates derived from the oxidation of the double bond (e.g. p-hydroxybenzaldehyde) were detected [18]. Thus, for p-coumaric acid cleavage of the double bond appears to be more likely than oxidative opening of the aromatic ring, while with p-hydroxyphenylacetic acid the ring opening reaction is largely favored.

4. Conclusions

As already observed for other families of contaminants present in olive oil wastewater, solar light and air are able to degrade p-hydroxyphenylacetic acid and tyrosol when pyrylium salts are present in the solution. Based on fluorescence quenching experiments, an electron transfer mechanism involving substrate-derived radical cation is proposed. This is also supported by detection of p-hydroxymandelic acid and p-hydroxybenzaldehyde as reaction intermediates.

Although the pyrylium salt-photocatalyzed process is less efficient than ozonization (with or without UV-irradiation), it is potentially more convenient from the environmental point of view.

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