Photochemistry and Photobiology, 2010, 86: 247–254

Reaction Pathways for the Photodegradation of the Organophosphorus Cyanophos in Aqueous Solutions

Matthieu Menager[1], Jean François Pilichowski[1,2] and Mohamed Sarakha*[1]

[1]Clermont Université, Université Blaise Pascal, Laboratoire de Photochimie Moléculaire et Macromoléculaire, UMR CNRS 6505, Clermont Ferrand, France
[2]CNRS, UMR 6505, Aubière, France

Received 12 June 2009, accepted 24 September 2009, DOI: 10.1111/j.1751-1097.2009.00654.x

ABSTRACT

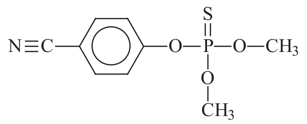
Photodegradation in aqueous solutions is an important pathway for many agrochemicals such as pesticides. In the present work, the photochemical transformation of cyanophos (CYA) was investigated in aqueous solutions using UV light within the 254–313 nm range as well as solar light. The study was performed in order to have a deep insight into the mechanistic pathways for the photochemical disappearance of CYA. Upon UV irradiation of an aerated solution of CYA, the degradation quantum yield was found equal to 1.8×10^{-2}. It is independent of the excitation wavelength but varies with oxygen concentration. It increased by a factor of 2 from oxygen-saturated to oxygen-free solution. Photosensitized experiments were performed using acrylamide and hydroquinone as energy acceptor and energy donor substrates, respectively. They show that both singlet and triplet excited states were involved in the photochemical behavior of CYA. The laser flash photolysis experiments clearly showed the involvement of the triplet excited state which was efficiently quenched by molecular oxygen and acrylamide with the rate constants 1.97×10^9 and 2.71×10^9 mol^{-1} L s^{-1}, respectively. The photoproducts structures were proposed according to the mass spectral data using the LC/MS technique. The analytical study shows that various processes such as hydrolysis, homolytic bond dissociations and Photo-Fries process occur.

INTRODUCTION

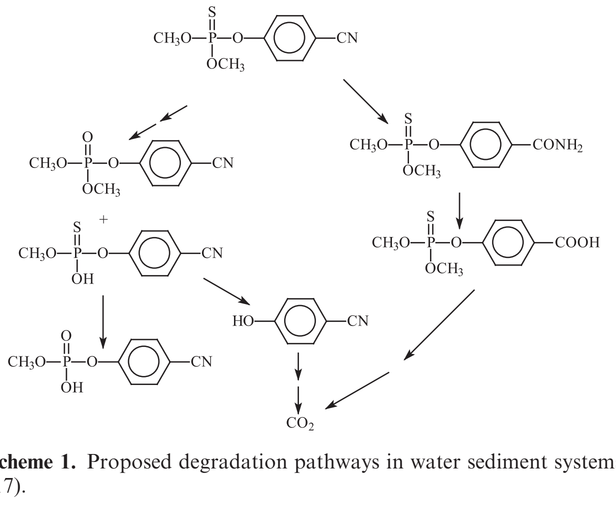
The increasing use of pesticides and other man-made chemicals represents the main cause of contamination of soils, ground and surface waters. As these compounds show a relatively high persistence, they may cause serious health and environmental problems that must be prevented and controlled (1–3). An important effort with great success has been made for the detection of these pollutants in the environment even at trace concentrations (4–8). However, the study of their fate and even their removal from environmental compartments appear to be urgent ecological problems which have to be seriously undertaken. Many of these pollutants, and more particularly pesticides which are present in aqueous solutions as well as at the surface of soils, can undergo photochemical transformation with solar light *via* direct and/or indirect photoreactions (9–13). It is then of great interest to know to what extent they can be degraded by such unavoidable processes and to elucidate the by-products that are photogenerated and which can be in some cases more harmful than the parent substrate. Several pesticides absorb solar light (λ > 295 nm) and can therefore undergo direct photochemical dissociation leading to the formation of various by-products. When the pollutant does not absorb solar light, it may still efficiently undergo photochemical transformations *via* indirect photoprocesses.

Cyanophos (O,O-dimethyl O-4-cyanophenyl phosphorothioate; CYA) is an insecticide from the organophosphorus family with a commercial name of Cyanox (14). Owing to its toxic level, its use is avoided in developing countries. It is already dropped from the list of some European countries.

Several studies have reported that such compounds are not easily hydrolyzed and thus they are highly persistent and accumulate in various aquatic compartments such as rivers and lakes (15,16). As shown in Scheme 1, the aerobic metabolism of CYA in water-sediment systems undergoes



Cynophos



Scheme 1. Proposed degradation pathways in water sediment systems (17).

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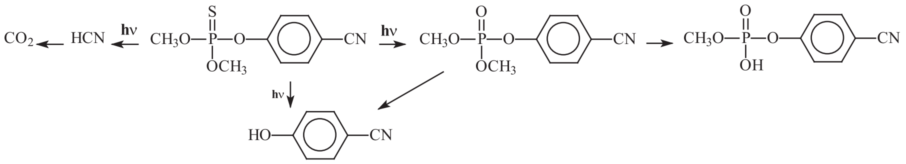
*Corresponding author email: mohamed.sarakha@univ-bpclermont.fr (Mohamed Sarakha)



Scheme 2. Photodecomposition pathways for Cyanox in silica and soil (18).

the cleavage of the P–O-methyl and P–O-aryl bonds together with the oxidation of the P = S to the oxon group and the hydrolysis of the cyano moiety (17).

From the photochemical point of view, some studies were performed on solid support such as silica and soil and in acetone solution (18). Under illumination, the half-life was estimated to be 2 and 4 days on soil and silica, respectively, while it was evaluated to be 120 min in acetone solution. Photo-oxidation reaction leading to the formation of the oxon derivative and the scission of the P–O bond generating 4-cyanophenol, as a major product, are reported to be the main observed processes (Scheme 2). To our knowledge, no detailed studies in aqueous solutions have been undertaken.

The present work was conducted in order to get a better insight into the photochemical behavior of CYA in aqueous solutions. The main goal was the study of the photochemical kinetic aspect by elucidating the nature of the by-products. The use of both conventional and time-resolving techniques will permit us to propose a detailed mechanism for the disappearance of CYA and the photogeneration of the products.

MATERIALS AND METHODS

Materials. CYA or (O-(4-cyanophenyl) O,O-dimethyl phosphoto-thioate) (98%) was purchased from Aldrich. Cyanophenol was from Jansen Chimica. Acrylamide and hydroquinone (> 99%) were provided by Aldrich. They were all used as received without further purification. All other reactants were of the highest grade available. The solutions were prepared with deionized ultra pure water which was purified with the Milli-Q device (Millipore) and its purity was controlled by its resistivity.

Steady-state irradiations. For kinetic as well as analytical purposes, aqueous solutions were irradiated with a parallel beam using a xenon arc lamp (1600 W) equipped with a Schoeffel monochromator. The bandwidth was 10 nm. Solution in a quartz cell (1 cm optical path length) was deoxygenated by argon or nitrogen bubbling or oxygenated by oxygen bubbling for 20 min prior to irradiation. The cell was then closed using a septum. The initial concentration of the solution was checked by HPLC analysis after bubbling. The irradiations at 254 nm were obtained with PHILIPS TUV 6 W lamp delivering a parallel beam. Potassium ferrioxalate was used as a chemical actinometer as reported in the literature (19). The pH of the solutions was adjusted using dilute solutions of $HClO_4$ or NaOH. For analytical purposes, irradiations were performed in a device equipped with germicide lamps (up to 6) emitting at 254 nm and a 100 mL cylindrical quartz reactor. A similar setup was used for the irradiation at 313 nm. Solar irradiation was performed in a quartz reactor (d = 1.5 cm) in Clermont-Ferrand (France, latitude 420° above sea level).

Laser flash photolysis. Transient absorption experiments in the 20 ns to 400 μs time scale were carried out on a nanosecond laser flash photolysis spectrometer from Applied Photophysics (LKS.60). Excitation (λ = 266 nm) was from the fourth harmonic of a Quanta Ray GCR 130-01 Nd:YAG laser (pulse width ≈5 ns), and was used in a right-angle geometry with respect to the monitoring light beam. A 3 cm^3 volume of an argon-saturated solution was used in a quartz cell, and was stirred after each flash irradiation. Individual cell samples were used for a maximum of five consecutive experiments. The transient absorbance at preselected wavelength was monitored by a detection system consisting of a pulsed xenon lamp (150 W), monochromator and a 1P28 photomultiplier. A spectrometer control unit was used for synchronizing the pulsed light source and programmable shutters with the laser output. This also housed the high-voltage power supply for the photomultiplier. The signal from the photomultiplier was digitized by a programmable digital oscilloscope (HP54522A). A 32-bit RISC-processor kinetic spectrometer workstation was used to analyze the digitized signal.

Analyses. UV–visible spectra were recorded on a Cary 300 scan (Varian) spectrophotometer. LC/MS studies were carried out with Q-TOF-Micro/water 2699 from the CRMP center at University Blaise Pascal. It is equipped with an electrospray ionization source (ESI) and a Waters photodiode array detector. Each single experiment permitted the simultaneous recording of both UV chromatogram at a preselected wavelength and an ESI-MS full scan. Data acquisition and processing were performed with the MassLynx NT 3.5 system. Chromatography was run using a Nucleosil column 100-5 C18 ec (250 × 4.6 mm, 5 μm). Samples (5–10 μL) were injected either directly or after evaporation of an appropriate volume of the solvent for better detection. The flow rate was 0.3 mL min^{-1} and the injected volume was 50 μL. The elution was accomplished with acidified water (acetic acid 0.4%) and acetonitrile using the following gradient mode: % acetonitrile (time): 2 (initial); 10 (10 min); 70 (35 min); 2 (42 min).

The consumption of CYA and the formation of the by-products were monitored by an analytical HPLC using an HP1050 apparatus equipped with a photodiode array detector. The experiments were performed by UV detection at either 230 or 250 nm and by using a reverse-phase Macherey Nagel column (Nucleodur C8, 250 mm × 4.6 mm, 5 μm). The following gradient program was used by employing acidified water (acetic acid 0.4%) (1) and acetonitrile (2) at 1 mL min^{-1}.

Time (min)	Initial	3	13	20	30
% A	95	80	80	5	95
% B	5	20	20	95	5

pH measurements were carried out with a JENWAY 3310 pH-meter equipped with an Ag/AgCl glass combination electrode 9102 Orion. The pH of the solutions was adjusted using dilute solutions of HCl or NaOH. The accuracy achieved was within ±0.01 pH units.

RESULTS

Steady-state irradiation studies

The absorption spectrum of CYA in aqueous solution shows two well-defined bands (Fig. 1). The short wavelength absorption band, attributed to a π–π* transition, presents an absorption maximum at 232 nm with a molar absorption coefficient of 14 000 mol^{-1} L cm^{-1}. The second band (λ_{max} = 266 nm and ϵ = 1200 mol^{-1} L cm^{-1}) is owing to an n-* transition and clearly extends to 320–330 nm permitting a non-negligible overlap with the solar emission spectrum. Thus, CYA may be degraded to a certain extent by direct excitation from solar light. It is worth noting that no obvious degradation of aqueous solution of CYA in the dark and at room temperature was observed within the 0.1–2.0 mmol L^{-1} range.

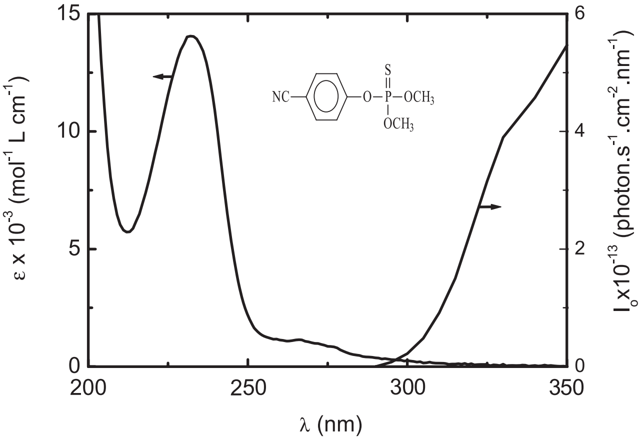


Figure 1. UV absorption spectrum of cyanophos in aqueous solution at pH = 5.4.

This suggests that dark processes such as hydrolysis are negligible in agreement with the literature (15,16).

Figure 2 gives the typical evolution of the absorption spectrum as a function of irradiation time when an aerated aqueous solution of CYA was exposed to light within the 254–313 nm range. It clearly shows a rapid decrease in the 232 nm band from the early stages of irradiation, indicating the disappearance of the pesticide. Moreover, owing to the formation of by-products, an increase in absorbance is also seen at $\lambda > 250$ nm.

The disappearance kinetics of CYA was further studied using HPLC. In all cases, the degradation process appeared to fit well the first-order kinetic model. As an example, under excitation at 254 nm (Fig. 2), the total disappearance was observed after roughly 6 h irradiation time with a half-life of 110 min. In air-saturated solutions, the disappearance quantum yield at 254 nm was evaluated at 1.8×10^{-2}. It was found to be independent of the initial concentration of the pesticide, of the pH of the solution and also of the excitation wavelength within the studied range (254–313 nm). Contrary to several other organophosphorus compounds (20,21), the latter result clearly demonstrates that the excitation within both bands, namely n–π* and π–π*, leads more likely to the same photochemical behavior.

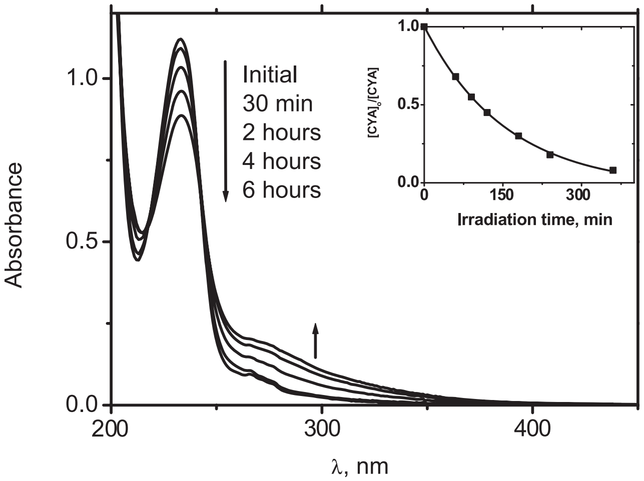


Figure 2. UV–Vis absorption changes observed for the irradiation of aerated solution of cyanophos (7.8×10^{-5} mol L^{-1}) upon irradiation with light in the 254–313 nm range at pH = 5.5. Inset shows the disappearance of cyanophos obtained by HPLC measurements as a function of irradiation time.

Table 1. Disappearance quantum yield of CYA as a function of oxygen concentration ([CYA] = 8.0×10^{-5} mol L^{-1}; pH = 5.4; $\lambda_{excitation}$ = 254 nm). The concentrations of oxygen were taken from Murov *et al.* (35).

[O$_2$] (mol L^{-1})	Disappearance quantum yield
1.27×10^{-3}	1.4×10^{-2}
2.7×10^{-4}	1.8×10^{-2}
$< 10^{-5}$	2.7×10^{-2}

The effect of oxygen concentration was also studied by bubbling either argon or oxygen. The determined quantum yields, gathered in Table 1, show that the photochemical reaction was partially inhibited by molecular oxygen. The quantum yield was lower by a factor of 2 from oxygen-free aqueous solution to oxygen-saturated solution. This clearly indicates that the two excited states, namely singlet and triplet excited states, are involved in the CYA photochemical process.

The irradiation of CYA was also realized using solar light and we found an efficient degradation. The complete disappearance occurred after 500 min in a sunny day.

Laser flash photolysis studies

In order to get a better insight into the transformation mechanism, we undertook nanosecond laser flash photolysis experiments. The laser excitation from the fourth harmonic (266 nm) of Nd:YAG laser of an argon-saturated aqueous solution of CYA (1.1×10^{-4} mol L^{-1}) at pH = 5.4 led to the formation of at least two short-lived transients (Fig. 3a).

The spectral features of solvated electrons were clearly observed at the end of the laser pulse, namely an absorption maximum at 720 nm (22,23). The absorption band was not observed when the solution was bubbled with N_2O, used as electron trap. As clearly shown in Fig. 3b, the amount of solvated electrons did not vary linearly with pulse energy showing that their formation, under our experimental conditions, is mainly through a biphotonic process. However, at the end of laser pulse in the presence of N_2O, a second short-lived transient was observed. It presents a band with a maximum located at 280 nm and two shoulders at 370 and 510 nm. Its absorbance increased linearly with laser energy, indicating its formation *via* a monophotonic process (Fig. 3b). The disappearance of this latter species followed a pseudo first-order kinetics with a rate that depended on oxygen concentration. In N_2O-saturated solution, the decay rate constant (k_{obs}) was found equal to 1.7×10^5 s^{-1} while it was evaluated at 7.6×10^5 and 2.7×10^6 s^{-1} in aerated and oxygen saturated solution, respectively. Such a transient reacts with oxygen as energy acceptor and it can more likely be attributed to the triplet excited state.

In order to obtain evidence for the formation of the triplet state in the photoreactivity of CYA, we used another energy acceptor substrate instead of oxygen. Acrylamide has largely been employed for this purpose in the literature (24,25). The laser excitation at 266 nm of an argon-saturated aqueous

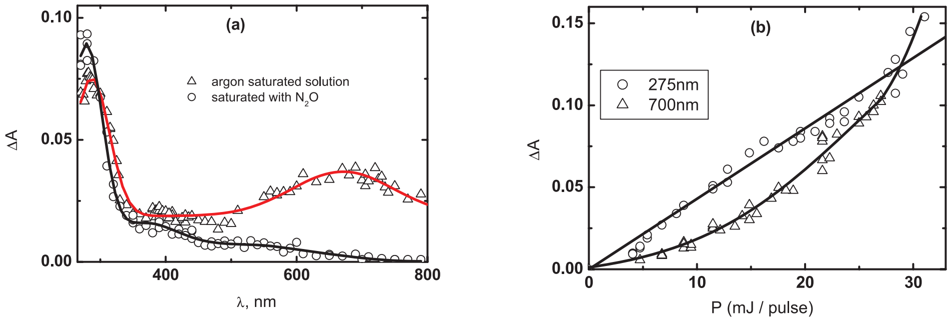


Figure 3. (a) Transient absorption spectra from an argon-saturated aqueous solution (Δ) and N_2O-saturated aqueous solution (○) of CYA under excitation at 266 nm (1.1×10^{-4} mol^{-1} L, pH = 5.4). (b) Evolution of the absorbance at 275 and 720 nm as a function of laser energy.

solution of the mixture acrylamide (2.0×10^{-3} mol L^{-1}) and CYA (1.1×10^{-4} mol L^{-1}) at pH = 5.4 led to a rapid decay of the absorbance at 275 nm, indicating that an energy transfer process is efficiently operating and that the triplet excited state was formed upon excitation of CYA.

The second-order rate constant for the reaction between molecular oxygen and the triplet excited state may be determined from the following kinetic plot:

$$k_{\mathrm{obs}} = k_{\mathrm{q}}[\mathrm{X}] + k_{\mathrm{o}}$$

where [X] represents the concentration of either oxygen or acrylamide, k_{obs} is the observed rate constant in the presence of a given concentration of X, k_{q} is the second-order rate constant for the energy transfer process and k_0 is the first-order rate for the decay of the triplet excited state in the absence of X.

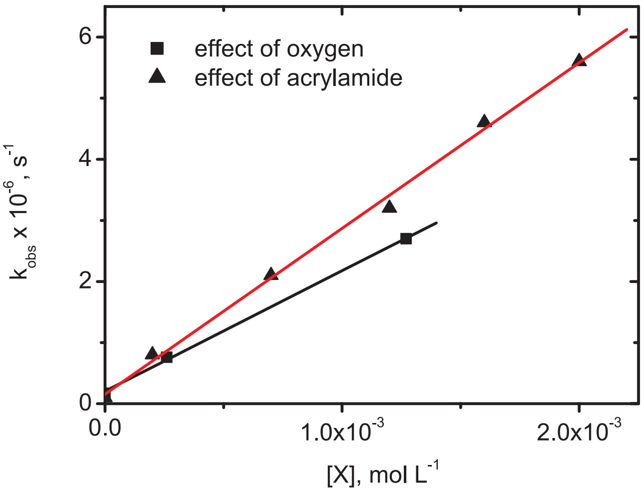


Figure 4. Evolution of the observed rate constant, k_{obs}, a function of either oxygen or acrylamide concentration (excitation at 266 nm; [CYA] = 1.1×10^{-4} mol L^{-1}, pH = 5.4).

As shown in Fig. 4, the plots k_{obs} as a function of [X] are linear and present a similar value of $k_{\mathrm{o}} = 1.7 \times 10^5$ s^{-1}. The second-order rate constant for the energy transfer process was found equal to 1.9×10^9 and 2.9×10^9 mol^{-1} L s^{-1} for molecular oxygen and acrylamide, respectively.

It is worth noting that in deaerated solution, the complete disappearance of the triplet excited state gave rise to a long-lived transient T_2. It presents an absorption band with a maximum at 400 nm (Fig. 5a) and disappears within 200 μs. Its concentration decreased by increasing the concentration of oxygen (Fig. 5b). This is in complete agreement with the fact that the triplet excited state is the precursor of T_2.

Photosensitized process

The photosensitized process through an energy transfer mechanism was further shown to occur using CYA as an energy acceptor and hydroquinone as a donor substrate (26,27). The latter compound was used as sensitizer as benzophenone and acetophenone were not sufficiently water soluble under our experimental conditions. Under excitation, hydroquinone is known to generate its triplet excited state with a quantum yield of 0.39 (28). Steady-state irradiation of hydroquinone (9.0×10^{-4} mol L^{-1}) using a monochromatic light at 300 nm in the presence of CYA (2.3×10^{-4} mol L^{-1}) was performed in aqueous solution. Under these experimental conditions, the light absorption is mainly owing to hydroquinone (λ_{max} = 286 nm). We observed an efficient disappearance of CYA indicating that the energy transfer from the triplet state of hydroquinone to that of CYA occurred. The

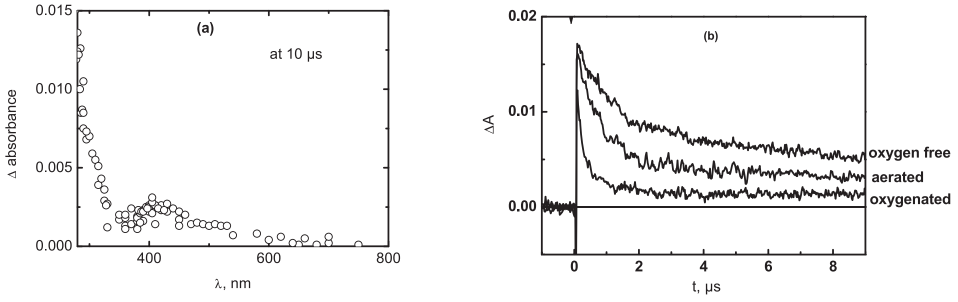


Figure 5. (a) Absorption spectra of T_2 recorded 10 μs after laser pulse. [CYA] = 1.1×10^{-4} mol L^{-1}, pH = 5.4, $\lambda_{\mathrm{excitation}}$ = 266 nm. (b) Evolution of absorbance at λ = 440 nm on 10 μs for various concentrations of oxygen. [CYA] = 1.1×10^{-4} mol L^{-1}, pH = 5.4, $\lambda_{\mathrm{excitation}}$ = 266 nm.

quantum yield of such energy transfer process was evaluated at 0.05.

Analytical studies

Several techniques were tested to track and to identify the stable products formed during the steady-state photolysis of CYA aqueous solutions, *e.g.* HPLC, HPLC/ESI/MS and NMR. Due to the nature of the pesticide used in this study, the latter technique was tested using ^{31}P-NMR but because of the limit of sensitivity at the employed concentrations, no significant results were obtained. Thus, the analytical studies were mainly performed by HPLC and HPLC/ESI/MS.

Aerated aqueous solutions of 80 μmol L^{-1} CYA were irradiated at 254 nm and analyzed by HPLC. A typical chromatogram obtained for about 30% conversion of CYA (Fig. 6) shows various stable by-products.

The same products were observed when the excitation was performed at 300 nm and also by using solar light. Their concentration increased as a function of irradiation time. The elucidation was realized by undertaking HPLC/ESI/MS experiments (with both ESI-negative and -positive modes). The system was equipped with a diode array system that permits to obtain the mass spectrum together with the absorption spectrum. It should be noted that as products P_2, P_3 and P_7 were observed in the initial solution and as their concentrations were unchanged or decreased during irradiation, they will not be discussed. Table 2 gathers the main fragments observed in the mass spectrum and the UV features of tentative degradation products.

P4 was identified as 4-cyanophenol. Its presence was further confirmed by using authentic samples. It roughly represents 15% of the CYA conversion. The formation of 4-cyanophenol appeared to depend on the concentration of oxygen: the higher the concentration of oxygen the higher the percentage of 4-cyanophenol obtained. The conversion was estimated to be 42% in oxygen-saturated solution. The irradiation of CYA in the presence of acrylamide gave a negligible effect on the amount of CYA. It is worth noting that the formation of 4-cyanophenol was negligible when the irradiation was performed in acetonitrile as a solvent instead of water. Thus, its formation mainly involves the singlet excited state more likely through a photohydrolysis process as shown with several types of organophosphorous pesticides (15,29,30). Such reaction may more likely occur through a heterolytic mechanism.

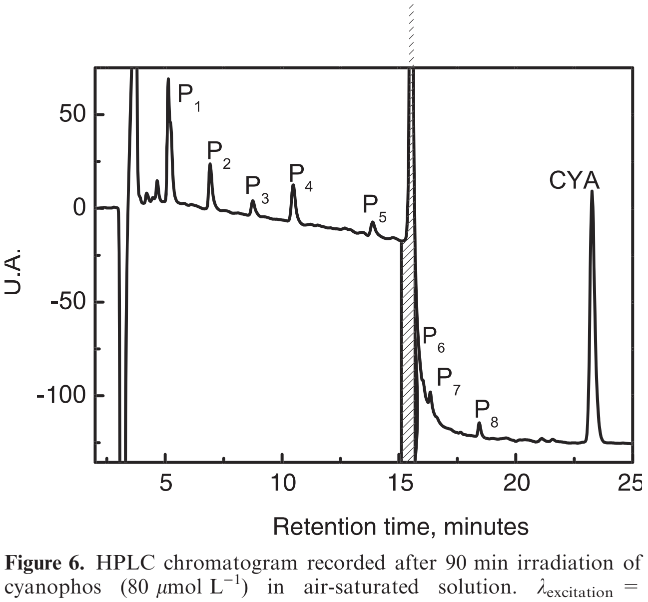
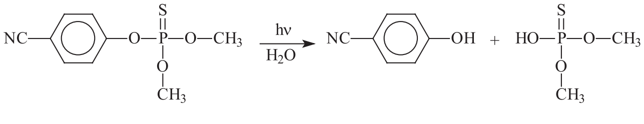
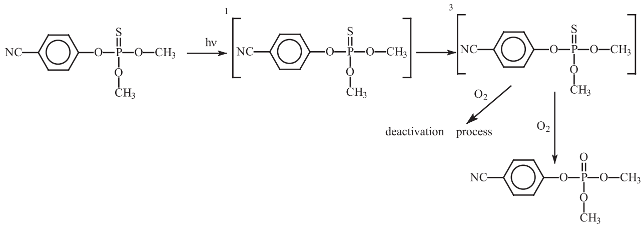


Figure 6. HPLC chromatogram recorded after 90 min irradiation of cyanophos (80 μmol L^{-1}) in air-saturated solution. $\lambda_{\text{excitation}}$ = 254 nm; pH = 5.4. The observed drift of the baseline is due to the used gradient program. Its shape was unchanged when water alone was injected.



The by-product P_5 presents an absorption spectrum similar to that of CYA. The molecular fragment, as well as some main fragments, is similar to those obtained in the case of CYA but with a difference of 16 units. This is in complete agreement with the substitution of the sulfur atom by an oxygen atom giving rise to the formation of the oxon derivative as largely observed with organophosphorus compounds (18,31). Under our experimental conditions, its formation is highly inhibited in the presence of oxygen and also in the presence of acrylamide showing that the triplet excited state is more likely involved. Such oxidative reaction occurs in competition with the deactivation of the triplet state by oxygen as demonstrated by laser flash photolysis studies.



The product P_6 presents a molecular mass similar to that of the initial compound CYA. It shows a different UV spectrum but a similar fragmentation in the ESI+ mode leading us to the conclusion that an isomer of CYA was formed. It is more likely generated *via* the singlet excited state as no effect of oxygen was observed. The experimental data clearly show that its formation involves a pathway different from that leading to the formation of 4-cyanophenol: (1) the rate of its formation does not depend

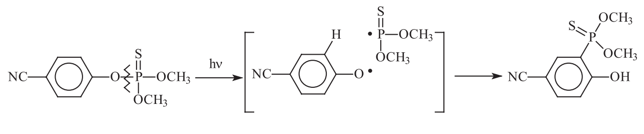
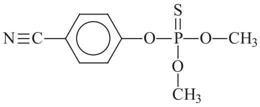
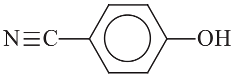
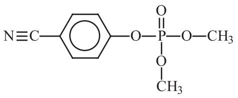
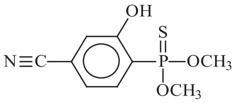
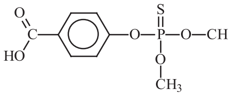


Table 2. Mass spectrum features and UV absorption maxima of tentative by-products obtained by UV irradiation of cyanophos in aqueous solution. The features of cyanophos are also given for comparison.

Chemical structure		R_t (min)	λ_{max} (nm)	$[M + H^+]$ with ESI+	$[M - H^+]$ with ESI−	Main fragments
CYA		23	233; 266	**244**	**242**	206; 175; 182; 162;154 228; 182; 166; 141
P_1	Not identified	5.1	232; 274	N.S.	**182**	118
P_4		10.6	246	N.S.	**188**	No fragmentation
P_5		13.8	232; 270	**228**	N.S.	190; 175; 166;154; 146
P_6		16	236; 255 (sh)	**244**	N.S.	182; 162; 154
P_8		18.5	236	N.S.	**261**	217; 141

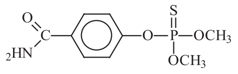
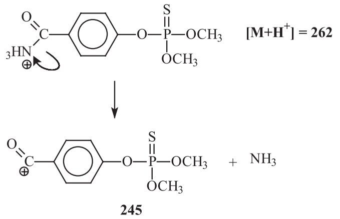
R_t = retention time; sh = shoulder. N.S. = no signal. The bold values refer to the molecular ion.

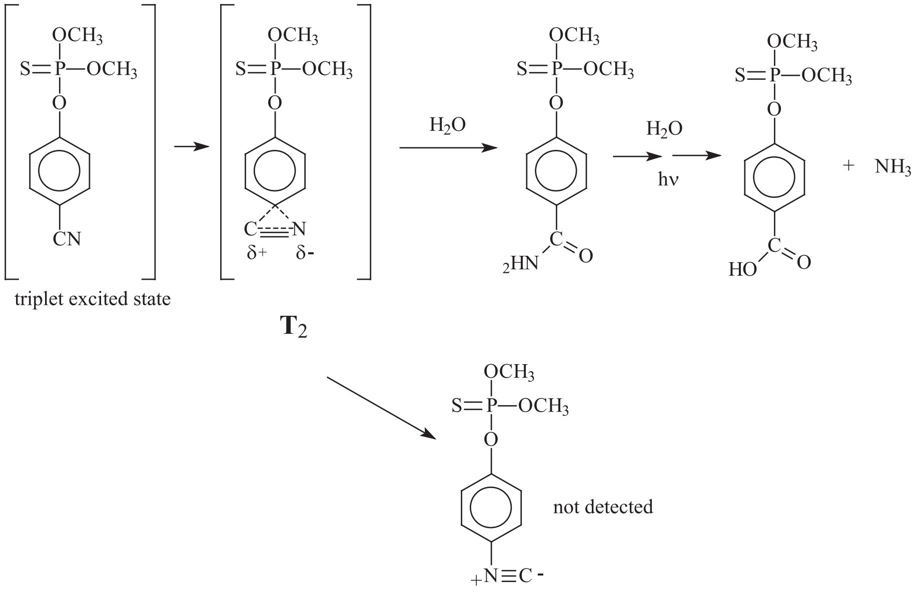
on acrylamide concentration and (2) its formation was not completely inhibited as acetonitrile was used as a solvent instead of water. In agreement with the results obtained with various other pesticides such as carbamates (32) and phenylureas (33) a photo-Fries type reaction through the homolytic dissociation of the P–O bond can be proposed.

The formation of P_8 involves the reactivity on the cyano group of the pesticide. The presence of the fragment ion at 217 is in agreement with a decarboxylation process as largely observed with carboxylic compounds. The formation of P_8 is arising from the triplet excited state pathway as it was totally absent when the irradiation was performed in the presence of oxygen as well as in the presence of acrylamide. It has to be pointed out that it represented the main by-product when the degradation was sensitized by excitation of hydroquinone at 300 nm. Moreover, while performing the sensitized experiments, a new product appeared to be present. It was identified on the basis of its mass spectrum. Its molecular fragment was found at 262 together with a unique fragment at 245. It was identified as O-(4-carbamoylphenyl) O,O dimethyl thiophosphate (Table 3).

The mechanism for the formation of these by-products may be drawn using the mechanistic study reported in the literature on 4-cyanophenol (34). The formation of a long-lived zwitterionic intermediate (T_2) arising from the triplet excited state, as observed from laser flash photolysis studies, followed by its hydrolysis may be the precursor of the carbamoyle derivative. The latter products may be further hydrolyzed or photolyzed as reported in various studies (17,34) to yield P_8. It is worth noting that in our study no photoisomerization into the benzoisonitrile derivative was observed, showing that it is not stable under our experimental conditions.

Table 3. Chemical structure and the elucidation of the fragment at 245.

 O-(4-carbamoylphenyl) O,O dimethyl thiophosphate	



CONCLUSION

The irradiation of the organophosphorus CYA with UV light $\lambda > 254$ nm as well as solar light led to an efficient disappearance of the pesticide. The process was shown to be partially dependent on oxygen concentration. Both singlet and triplet excited states were involved. The degradation of CYA was further demonstrated by using hydroquinone as photosensitizer. The light excitation of CYA permitted the formation of various by-products *via* oxidation, hydrolysis, homolytic dissociations and photo-Fries processes. The oxidation reaction leads to the formation of the highly toxic oxon derivative.

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