Supporting information

Photoreactivity of the fungicide chlorothalonil in aqueous medium

Samira Bouchama[1,2], Pascal de Sainte-Claire[1,3], Emmanuel Arzoumanian[4], Esther Oliveros[4], Abdelaziz Boulkamh[2], Claire Richard[1,5*]

[1] Clermont Université, Institut de Chimie de Clermont-Ferrand, BP 10448, 63000 Clermont-Ferrand, France.

[2] Laboratoire des Techniques Innovantes de Protection de l'Environnement, Université de Constantine 1, Route de Aïn-el-Bey, 25000 Constantine, Algérie.

[3] Clermont Université, ENSCCF, Institut de Chimie de Clermont-Ferrand, BP 10448, 63000 Clermont-Ferrand, France.

[4] Laboratoire des IMRCP, UMR CNRS 5623, Université Toulouse III (Paul Sabatier, UPS), 31062 Toulouse Cedex 9, France.

[5] Equipe Photochimie CNRS, UMR 6296, ICCF, F-63171 Aubière, France.

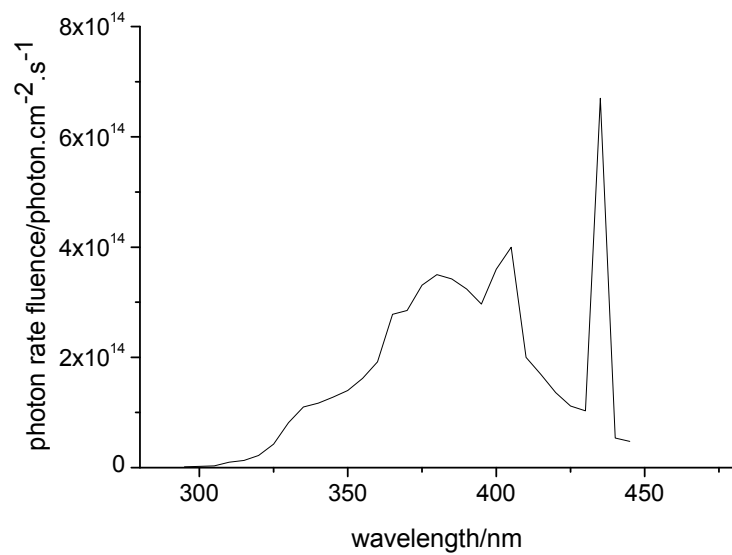Figure SI-1: Emission spectrum of the fluorescent tubes

Figure SI-2: Absorption spectrum of CT (5×10^{-6} M) in acetonitrile/water pH 8 (5:95, v/v) in a cell of 2-cm path
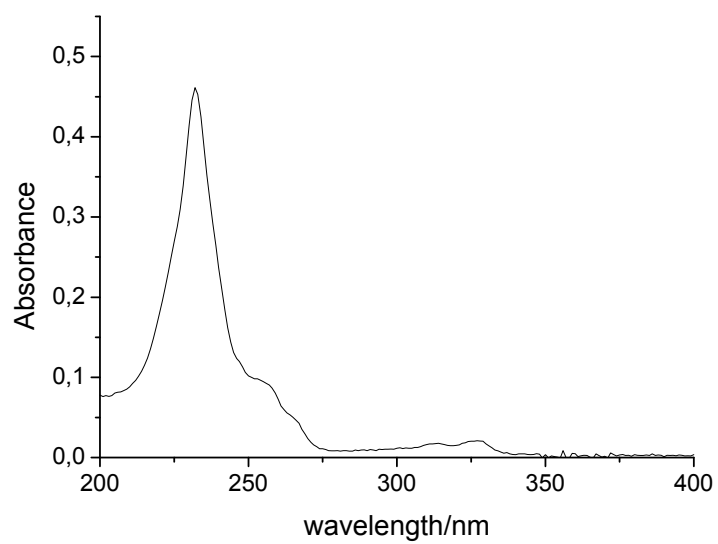
Figure SI-3: Absorption spectrum of an aerated CT solution in 50% ACN, before (black line) and after (red line) irradiation.
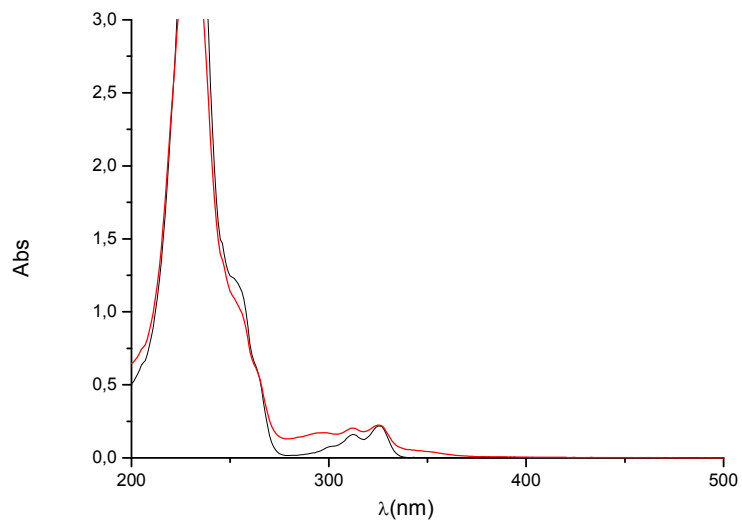

Figure SI-4 : Influence of the percentage of acetonitrile on k_d^{aerated}
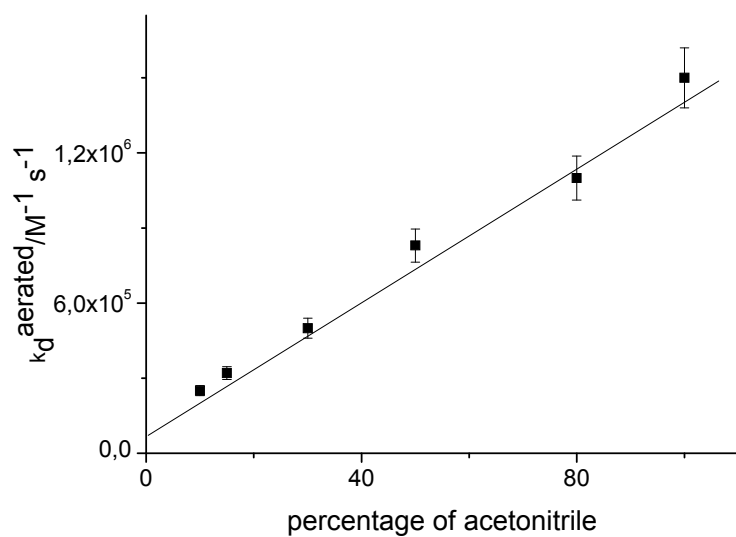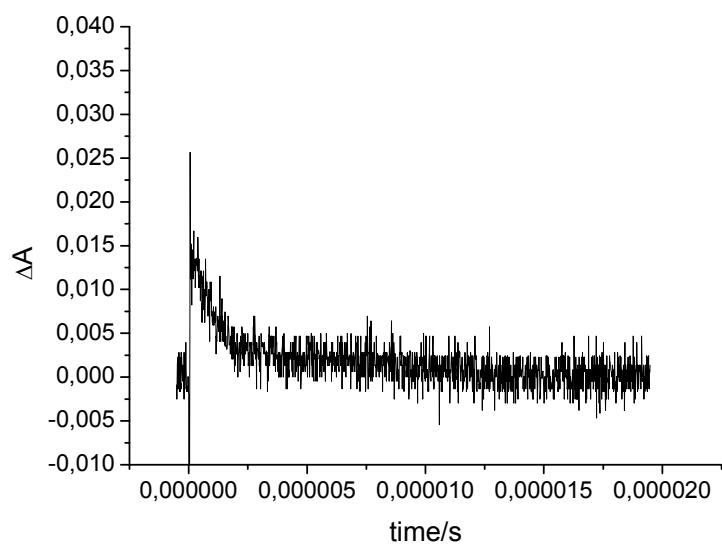
Figure SI-5: Absorbance profile measured at 320 nm upon irradiation of CT in isopropanol

Singlet oxygen measurements

The quantum yields of $^1O_2$ production (Φ_Δ) were determined by recording the $^1O_2$ emission signal upon continuous monochromatic excitation of the sensitizer[1-3]. PN is a standard singlet oxygen sensitizer with a Φ_Δ^{PN} close to 1 in a large variety of solvents[4-7] and was chosen as a reference in this work.

Wavelengths of 367 nm and 313 nm were chosen to irradiate solutions of PN and CT respectively. Under continuous irradiation, the quantum yield of $^1O_2$ emission is given by:

$$\Phi_e = C\,S_e\,P_a \qquad (1)$$

where C is a proportionality factor depending on geometric and electronic characteristics of the detection system and on specific parameters of the medium (refractive index, NIR absorbance), S_e is the $^1O_2$ signal intensity, P_a that is equal to $P_0(1-10^{-A})$ is the photon flux absorbed by the sensitizer (P_0 and A are the incident photon flux and the absorbance of the sensitizer at the wavelength of excitation, respectively). Φ_e may be also expressed as:

$$\Phi_e = \Phi_\Delta\,k_e\,\tau_\Delta \qquad (2)$$

where k_e is the rate constant of $^1O_2$ emission and τ_Δ the $^1O_2$ lifetime. In the absence of quencher one has:

$$\tau_\Delta = 1/k_d \qquad (3)$$

with k_d, rate constant in s^{-1} of $^1O_2$ deactivation by the solvent, k_e and k_d being medium dependent and $k_e \ll k_d$ in most solvents.[8-10] while in the presence of a quencher (Q) that may be the sensitizer itself, one has:

$$\tau_\Delta = \frac{1}{(k_d + k_t^Q[Q])} \qquad (4)$$

The rate constant of $^1O_2$ total quenching (physical and reactive quenching) (k_t^{CT}) and the quantum yield of $^1O_2$ production (Φ_Δ) by CT were determined by relative measurements,

using PN as a reference sensitizer. Combining eqns. (1) to (4), the ratio of the $^1O_2$ luminescence quantum yields for CT and PN in the same solvent is given by:

$$\frac{\Phi_e}{\Phi_e^{PN}} = \frac{\Phi_\Delta}{\Phi_\Delta^{PN}} \frac{k_d + k_t^{PN}[PN]}{k_d + k_t^{CT}[CT]} = \frac{CS_e}{C_{PN}S_e^{PN}} \frac{P_0^R(1 - 10^{-A(\lambda_{PN})})}{P_0(1 - 10^{-A(\lambda)})} \tag{5}$$

where Φ_Δ^{PN} and Φ_Δ are, respectively, the quantum yields of $^1O_2$ production by the reference sensitizer (PN) and CT. The determination of $\frac{\Phi_\Delta}{\Phi_\Delta^{PN}}$ and of k_t^{CT} is possible when the following conditions are satisfied:

- The absorbance of the sample and reference are the same at the corresponding wavelengths of excitation (λ and λ_{PN}) : in this case, the absorption factors (1-10^{-A}) and the apparatus factor (C) remain identical in both systems;

- The reference sensitizer (PN) is chosen so that $k_t^{PN}[PN] \ll k_d$. Within the limits of error, the ratio $\frac{S_e^{PN}}{S_e^{CT}} \frac{(1-10^{-A(\lambda)})}{(1-10^{-A(\lambda_{PN})})} \frac{P_0}{P_0^{PN}}$ does not significantly change in the studied domain of CT concentrations. Therefore, we conclude that the product $k_t^{Sens}[Sens] \ll k_d$.

When these conditions are fulfilled, eqn. (5) simplifies to eqn. (6):

$$\frac{S_e^{PN}}{S_e^{CT}} = \frac{P_0^{PN}}{P_0} \frac{\Phi_\Delta^{PN}}{\Phi_\Delta} (1 + \tau_\Delta k_t^{CT}[CT]) \tag{6}$$

and the plot of $\frac{S_e^{PN}}{S_e^{CT}} = f([CT])$ should be linear. Thus, values of k_t^{CT} and $\frac{\Phi_\Delta^{PN}}{\Phi_\Delta}$ may be obtained from the slope and the intercept of this plot if the value of τ_Δ is known. In our case, probe and reference were irradiated at different wavelengths (313 nm and 367 nm respectively) and $\frac{P_0^{PN}}{P_0} = 1.88$.

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Table SI-1. Values of S_e^{PN}, S_e^{CT}, $\frac{S_e^{PN}}{S_e^{CT}} \frac{(1-10^{-A(\lambda)})}{(1-10^{-A(\lambda_{PN})})} \frac{P_0}{P_0^{PN}}$ and Φ_Δ in solutions with different percentages of acetonitrile (100, 80, 50 and 30) in acetonitrile/D_2O mixtures.

	A^{PN} (367 nm)	S_e^{PN} (a.u.)	A^{CT} (313 nm)	S_e^{CT} (a.u.)	$\frac{S_e^{PN}}{S_e^{CT}} \frac{(1-10^{-A(\lambda)})}{(1-10^{-A(\lambda_{PN})})} \frac{P_0}{P_0^{PN}}$	Φ_Δ
100 % ACN	0.82	124	0.82	58	0.88	0.85 ±0.06
	0.6	114	0.67	52	0.82	
	0.41	72	0.41	35	0.91	
	0.2	41	0.26	21	0.79	
80 % ACN	0.86	132	0.94	64	0.89	0.85 ±0.04
	0.63	105	0.7	51	0.87	
	0.42	79	0.48	39	0.86	
	0.2	43	0.26	22	0.79	
50 % ACN	0.88	86	0.91	40	0.87	0.85 ±0.02
	0.67	83	0.64	37	0.85	
	0.42	49	0.38	20	0.82	
	0.22	34.5	0.21	15	0.85	
30% ACN	0.33	36	0.35	12	0.6	0.69 ±0.08
	0.22	26	0.25	10.5	0.69	
	0.11	14	0.14	7	0.76	