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Reactive Oxygen Species (ROS)-vs peroxy-mediated photosensitized oxidation of triphenylphosphine. A comparative study.

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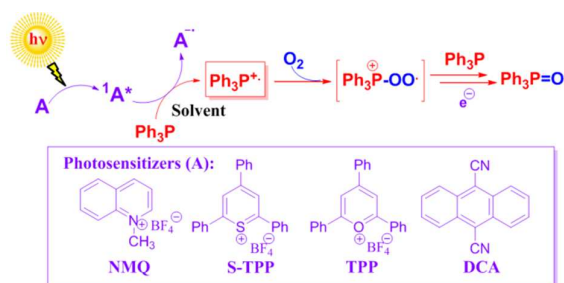
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Table of Contents/Abstract Graphic.



Abstract. The oxidation of triphenylphosphine in the presence of various photocatalytic systems (dicyanoanthracene/biphenyl, *N*-methylquinolinium, triphenylpyrylium and thiatriphenylpyryliumtetrafluoroborate) was investigated by means of both steady state and laser flash photolysis experiments. The effect of different additives (including 1,4-benzoquinone, diphenylsulfoxide, tetramethylethylene and sodium azides) on the photosensitized oxidation was investigated in order to fully characterize the involved intermediates. Photoinduced electron transfer and final regeneration of the catalyst occur when dicyanoanthracene and *N*-methylquinolinium are used, while *in cage* oxygen transfer to the photoexcited (thio)pyrylium derivatives have been characterized in the last two cases.

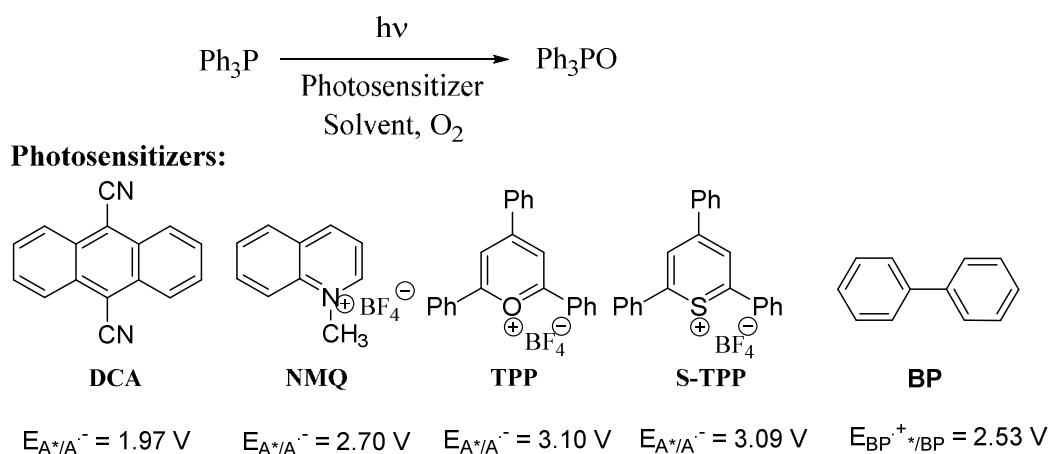
INTRODUCTION

Molecular oxygen ($^3\text{O}_2$) is the ideal reagent for sustainable oxygenation processes because of its abundant availability and its nontoxicity.¹ Since direct concerted addition of (singlet) organic molecules and triplet oxygen ($^3\text{O}_2$) is a spin-forbidden process, activation of at least one of the reagents is required. Activation of molecular oxygen can occur either via transition metal photocatalysis² or by using a suitable photocatalyst to produce singlet oxygen ($^1\text{O}_2$) via sensitization in a spin-allowed process³ or odd electron species (either Reactive Oxygen Species, ROS, or radicals or radical ions from the organic molecules) via photoinduced electron transfer.⁴ It is not always easy to recognize the mechanism involved in any specific case and actually oxidizable molecules may react through a variety of paths according to conditions. Although metal complexes are increasingly used in photocatalyzed reactions, organic photocatalyst/sensitizers still offers a promising alternative and the mechanism is often more easily characterized. Apart from organic dyes, largely used organic compounds used in this capacity include heteroaromatic cations (pyrylium and thiapyrylium,⁵ quinolinium⁶ and acridinium salts⁷) as well as aromatic nitriles,⁸ due to their high one-electron oxidation potential from the low-lying excited state (either singlet or triplet). Among oxidizable substrates, aliphatic and aromatic sulfides have been largely studied,⁹ and a variety of different mechanisms have been demonstrated to be involved. Another class of electron donors that have been deeply investigated is that of triarylphosphines [for the parent molecule, $E_{\text{ox}}(\text{Ar}_3\text{P}/\text{Ar}_3\text{P}^+)=1.00\text{V}$]¹⁰ and are of interest as excellent electron donors. The radical cation then evolved to a stable photoproduct, the phosphine oxide ($\text{Ar}_3\text{P}=\text{O}$). This intermediate exhibits a dual reactivity, as an electrophile (in the presence of different nucleophiles such as alcohols, water, halides, hydroxyl anions and bases¹¹) as well as a free radical (with thiols).¹²

It thus seemed appropriate to choose the easily oxidized triphenylphosphine as a probe for comparing the photooxidation by various photocatalysts and look for experimental support for the mechanism. We report below a combined steady state and time resolved investigation by using four different sensitizers, viz 9,10-dicyanoanthracene (DCA, E^* vs SCE = 1.97 V),¹³ *N*-

methylquinolinium (NMQ, E^* vs. SCE = 2.70 V),¹³ 2,4,6-triphenylpyrylium (TPP, E^* vs. SCE = 3.10 V for the singlet excited state)¹⁴ and 2,4,6-triphenylthiapyrylium (S-TPP, E^* vs. SCE = 3.09 V for the singlet excited state)¹⁵ in different solvents (CH_2Cl_2 , MeCN, MeOH and MeCN/Water 9/1 mixture, Scheme 1). With the photocatalysts used oxidation of triphenylphosphine is in every case an exergonic process ($\Delta G = -22.4 \text{ Kcal mol}^{-1}$ for DCA; $-62.3 \text{ Kcal mol}^{-1}$ for NMQ; $-48.4 \text{ Kcal mol}^{-1}$ for TPP and $-48.2 \text{ Kcal mol}^{-1}$ for S-TPP). In the case of DCA, the use of biphenyl as co-sensitizer was used to improve the process, as previously observed by Majima and co-workers.¹⁶

Scheme 1. Photosensitized oxidation reaction of triphenylphosphine and chemical structures of the photosensitizers.



RESULTS

Fluorescence quenching. The fluorescence parameters of the photocatalysts considered have been recently collected in a review by Miranda and co-workers.¹⁷ DCA, NMQ and TPP exhibit a medium to high fluorescence quantum yield (from 0.47 to 0.90) in acetonitrile, whereas S-TPP shows a significantly lower emission ($\Phi_F = 0.06$). In every case, the fluorescence quenching by triphenylphosphine occurred efficiently (k_q ranging from 1.9 to $7.9 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ see Table 1).

Table 1. Fluorescence quantum yield, fluorescence lifetime and rate constants for the quenching (k_q) of the photocatalysts used by Ph_3P in MeCN.

Photosensitizer	Φ_F^a	τ / ns	$k_q / \text{M}^{-1}\text{s}^{-1}$
DCA	0.90	15.3 ^b	1.9×10^{10}
NMQ	0.85	20 ^c	2.2×10^{10}
TPP	0.47	2.9 ^d	7.9×10^{10}
S-TPP	0.06	3.1 ^e	5.1×10^{10}

^a From ref 17. ^b From ref. 18. ^c From ref. 19. ^d From ref. 5d. ^e From ref. 20.

Photochemical reactions. The irradiation of O_2 -saturated solutions of Ph_3P in the presence of the photocatalysts gave phosphine oxide as the only stable product when the reaction mixture was analyzed by GC. In every case, the sum of the amounts of Ph_3P and Ph_3PO accounted for more than 90% of the material balance. No other product was detected by the GC. Irradiations were performed at 410 nm (multilamp reactor, 4 lamps), except for NMQ, where the same reactor with lamps emitting at $\lambda = 365$ nm has been used, due to the negligible absorbance of this photocatalyst at 410 nm. The quantum yield of photo oxidation of a PPh_3 solution (0.011 M) was measured in different solvents in the presence of a chosen photocatalyst (10^{-3}M , with the exception of DCA, for which a concentration of 10^{-5} M was used). The effect of some additives (1,4-dimethoxybenzene (DMB), 1,4-benzoquinone (BQ) and diphenylsulfone (Ph_2SO)) on the irradiation was likewise explored. In every case, the oxidation rate was strongly reduced in oxygen-free solutions. The results thus obtained have been summarized in Tables 2 and 3.

Table 2. Quantum yield of consumption of Ph₃P with different photosensitizers.

Solvent	ϕ^a			
	DCA ^b	NMQ ^c	TPP	S-TPP
MeCN	0.033	0.143	0.019	0.184
MeCN (N ₂)	< 1×10 ⁻³	0.013	0.007	0.009
MeOH	0.015	0.056	0.090	0.091
DCE	0.023	0.169	0.048	0.103
MeCN – H ₂ O (9:1)	0.007	0.128	0.077	0.265

^a[Ph₃P]: 0,011 M; [Photosensitizer]: 1.0×10⁻³ M; λ_{exc} : 410 nm. ^b[DCA]: 1×10⁻⁵ M (in the presence of biphenyl 10⁻²M as co-sensitizer). ^c λ_{exc} : 365 nm. All data were obtained with a ± 0.001 error

Table 3. Rate of Ph₃PO [$\mu\text{mol}\cdot\text{min}^{-1}$] formation in the presence of different photocatalysts and additives.^a

	DCA				NMQ			
	None	DMB ^b	BQ ^c	Ph ₂ SO ^d	None	DMB	BQ	Ph ₂ SO
MeCN	1.40	1.49	0.89	1.34	9.6	6.6	4.8	9.6
MeOH	1.81	1.53	1.05	1.66	6.0	4.8	3.6	7.2
DCE	2.88	2.73	1.96	1.10	11.4	11.4	2.4	12.6
	TPP				S-TPP			
MeCN	9.0	7.2	6.6	10.8	11.4	11.4	7.2	10.2
MeOH	6.0	5.4	3.0	6.0	3.6	3.6	3.0	4.8
DCE	5.4	4.8	4.8	5.4	4.2	4.2	4.8	4.2

^aAmounts of triphenylphosphineoxide formed in $\mu\text{mol}\cdot\text{min}^{-1}$. ^b5×10⁻² M 1,4-dimethoxybenzene (DMB). ^c1.25×10⁻³ M 1,4-Benzoquinone (BQ). ^d2.5×10⁻³ M Ph₂SO.

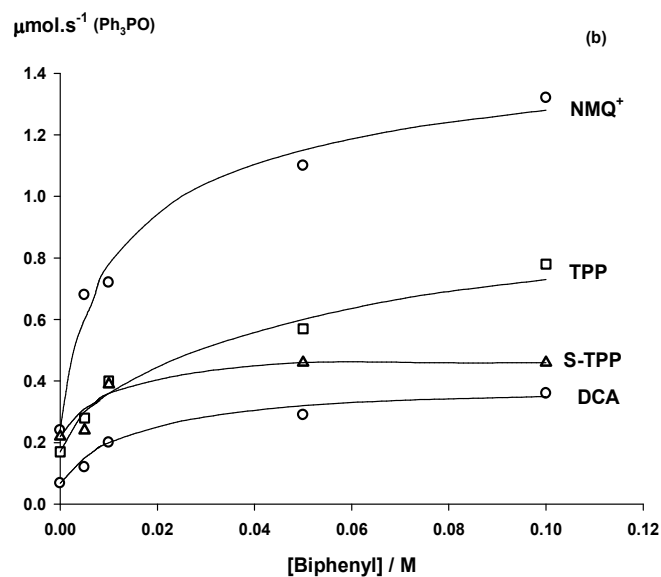
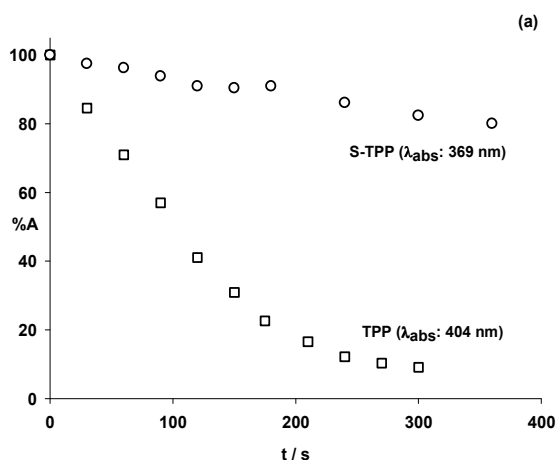
1 *Photocatalyzed oxidation via DCA.* Consistent with what was observed in previous reports,^{5e, 17} the
2 DCA/Biphenyl photosensitized oxidation of Ph₃P was found to be quite inefficient ($\Phi < 0.05$). The
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4 use of a protic environment further lowered the reaction efficiency (from $\Phi = 0.033$ to 0.015 when
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6 moving from neat acetonitrile to methanol). The oxidation rate was not unaffected by the presence
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8 of 1,4-dimethoxybenzene (DMB), whereas the quenching effect of diphenylsulfoxide (Ph₂SO) was
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10 found to be significant only in dichloromethane solution, where the oxidation rate decreased from
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12 2.88 to 1.10 $\mu\text{mol min}^{-1}$. The addition of 1,4-benzoquinone reduced the rate value of *ca.* one third in
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14 all of the systems tested.
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20 *Photocatalyzed reactions via NMQ.* With NMQ as the photosensitizer, the oxidation quantum
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22 yields improved, with maximal values in polar aprotic solvents (up to 0.169 in dichloromethane). In
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24 the absence of oxygen, the photo oxidation rate was decreased to one tenth of the initial value.
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26 Again, the use of a protic medium resulted in a lowering of the quantum yield value. As for
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28 quenchers, DMB and Ph₂SO had little or no effect on the rate of phosphine oxide formation, while
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30 the use of BQ generally led to a significant decrease of the rate value, as previously observed with
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32 DCA.
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36 *Photocatalyzed reactions via TPP and S-TPP.* With the heterocyclic salts TPP and S-TPP as the
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38 photocatalysts the oxidation quantum yield varied from 2 to 9% with the former (maximal value in
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40 methanol and in dichloromethane) and from 9 to 26.5% with the latter (maximal value in
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42 acetonitrile-water 9:1). None of the above additives caused a large effect, with some slowing down
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44 of the reaction only with BQ in the oxidation in polar solvents.
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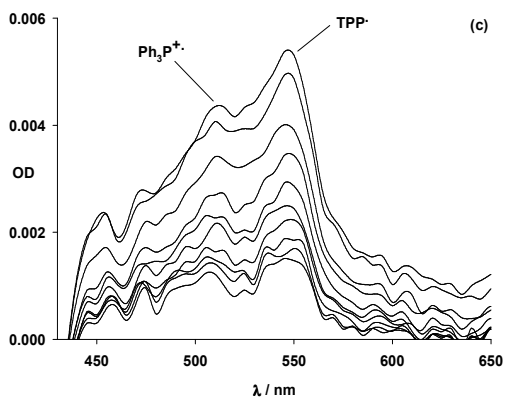
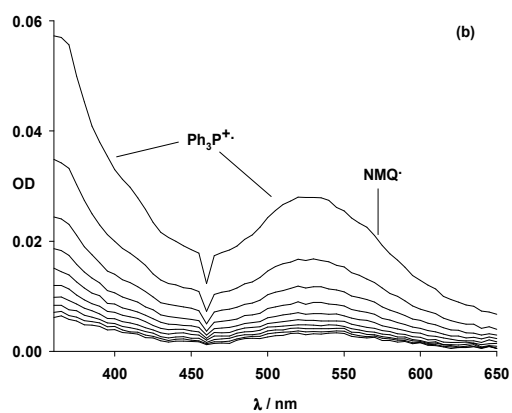
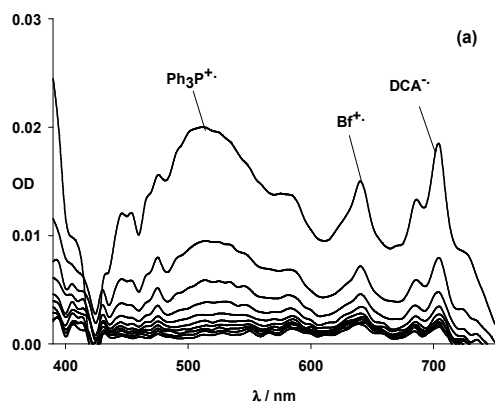
47 However, these photocatalysts were partially consumed during the irradiation in oxygen saturated
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49 nucleophilic media, such as MeOH, MeCN and aqueous MeCN solutions of the phosphine (see an
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51 example in Figure(1a)). The formation of Ph₃PO remained quantitative, though. In fact,
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53 photosensitization of Ph₃P with TPP in O₂-saturated MeCN – H₂O (9:1) at 405 nm on an optical
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55 bench provides 95 % yield of Ph₃PO at a fixed reaction time while TPP is only consumed in 23 %
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2 yield. Likewise, with S-TPP Ph_3PO is formed in 92 % yield while S-TPP is consumed in only 3 %
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4 yield. Finally, no significant consumption of both TPP and S-TPP was observed in apolar solvents.
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6 The use of biphenyl as a co-oxidant of all of the examined catalysts has been also considered.
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8 Interestingly, an enhancement of the photo oxidation rate has been observed with all of the
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10 photosensitizers used, with a maximum increase in the case of NMQ, for which the oxidation rate
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12 increased by a factor of five (Figure 1b).
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2 **Figure 1.(a)** Relative consumption of photosensitizers TPP and S-TPP during irradiation with λ_{exc} :
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4 405 nm of O₂-saturated solutions of PPh₃ (0.010 M) in MeCN – H₂O (9:1).**(b)** Effect of addition of
5
6 biphenyl on the photosensitized oxidation of O₂-saturated acetonitrile solution of PPh₃ (0.010 M).
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12 **Time-resolved spectroscopic measurements.** The steady state irradiations have been supplemented
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14 by laser flash photolysis experiments. The spectra obtained in the DCA/biphenyl system in the
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16 presence of PPh₃ clearly show the formation of three different absorption bands located at 530 nm,
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18 600 nm and 730 nm (Figure 2a). In accord with the literature¹⁸ we assigned the last two bands to the
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20 biphenyl radical cation (BP^{•+}) and DCA^{•-}, respectively. Similar results were obtained with the other
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22 photocatalysts in all of the chosen media. In all of the cases studied, formation of the two absorption
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24 bands located at 380 and 530 nm was observed but, due to the interference of other intermediates
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26 involved, only the former band was clearly visible in the presence of NMQ (Figure 2b).
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28 Experiments in the presence of sodium azide showed that both absorption bands were quenched by
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30 azide anion with similar k_q values ($k_q = 2.4\text{-}2.8 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$). Therefore, these bands can be
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32 univocally assigned to the absorption spectrum of a single transient, the triphenylphosphine radical
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34 cation (PPh₃^{•+}). Likewise, the reduced forms of the photo-oxidants (the corresponding *N*-
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36 methylquinolyl, pyryl and thiapyryl radicals) were also detected along with the transient radical
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38 cation. Representative examples are shown in Figure 2 for MeCN.
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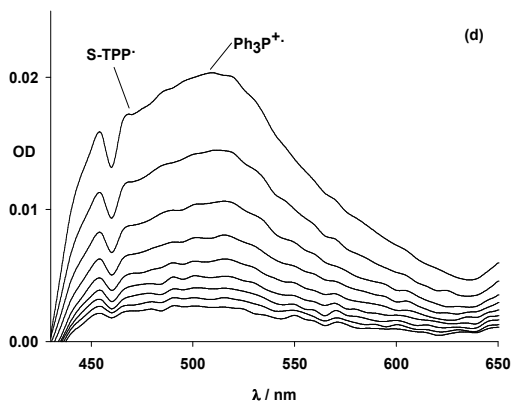
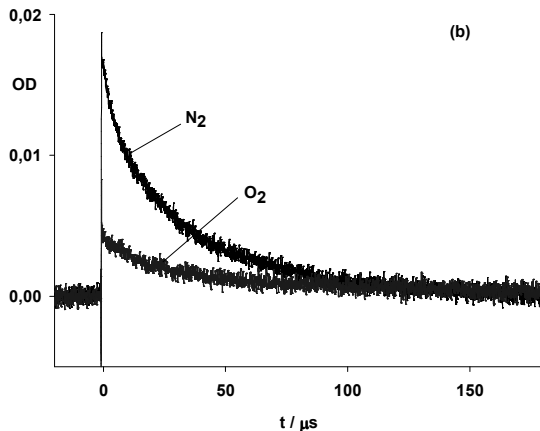
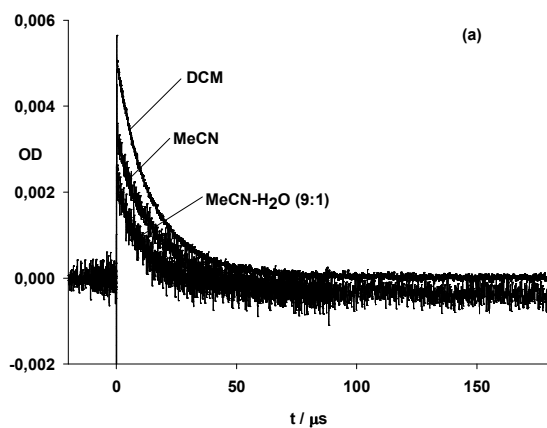


Figure 2. Transients absorption spectra recorded after a laser pulse (10 μs, λ_{exc} : 355 nm) of N₂-saturated acetonitrile solution of PPh₃ (0.0110 M) in the presence of: **(a)** DCA and BP; **(b)** NMQ; **(c)** TPP and **(d)** S-TPP.

The transient Ph₃P⁺ was found to decay with a second-order rate constant (k_2) of $10^9 - 10^{10} \text{ M}^{-1}\text{s}^{-1}$ (see Table 4) in N₂-saturated solution, whereas in O₂-saturated solution a pseudo-first-order decay was observed. In the latter case, a second-order rate constant of $10^9 - 10^{10} \text{ M}^{-1}\text{s}^{-1}$ was calculated by considering the concentration of O₂ solubilized in each of the solvents used. Representative decay curves of transient PPh₃⁺ in N₂- and O₂-saturated solutions are shown in Figure 3 for S-TPP and NMQ photosensitization. It should be noticed that triphenylphosphine oxide is the only photoproduct formed in the Ph₃P/TPP system after flashing the oxygenated solution with a laser pulse (λ_{exc} : 355 nm; 10 consecutive shots). Analogous results have also been obtained with the other sensitizers.



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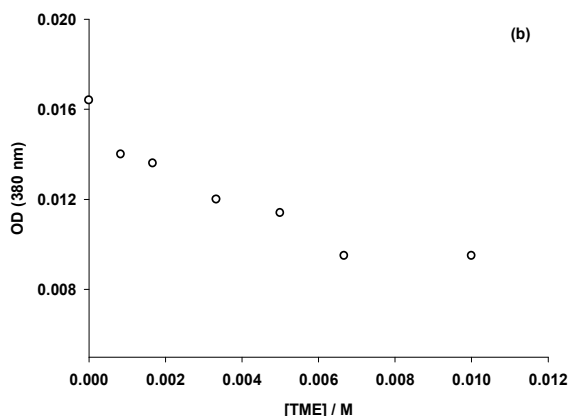
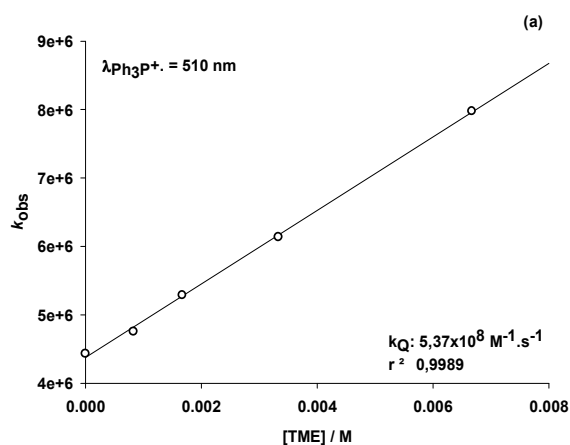
Figure 3.(a) Decay traces of PPh_3^+ after a laser pulse (λ_{exc} : 355 nm) of N_2 -saturated solutions of PPh_3 ($0.010 \text{ mol} \cdot \text{dm}^{-3}$) and NMQ ($1.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$) in dichloromethane, MeCN and MeCN- H_2O 9:1 mixture recorded at 510 nm. (b) Decay traces of PPh_3^+ after a laser pulse (λ_{exc} : 355 nm) of N_2 - and O_2 -saturated acetonitrile solutions of PPh_3 ($0.010 \text{ mol} \cdot \text{dm}^{-3}$) and S-TPP ($1.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$) recorded at 510 nm.

Table 4. Second-order decay parameters of Ph_3P^+ sensitized by DCA, TPP, S-TPP and NMQ in N_2 - and O_2 -saturated organic solvents.

		$k_2 / \text{M}^{-1} \cdot \text{s}^{-1}$			
Solvent	Atmosphere	DCA	NMQ	TPP	S-TPP
MeCN	N_2	1.6×10^{10}	3.4×10^{10}	7.3×10^9	1.6×10^{10}
	O_2^a	2.8×10^{10}	1.6×10^{10}	2.4×10^{10}	8.9×10^9
MeOH	N_2	1.7×10^{10}	Not deter.	3.4×10^9	1.6×10^{10}
	O_2^a	6.0×10^{10}	Not deter.	1.1×10^{10}	1.5×10^{10}
DCM	N_2	2.5×10^{10}	5.6×10^9	1.7×10^{10}	3.7×10^{10}
	O_2^a	1.4×10^{10}	2.0×10^{10}	4.9×10^{10}	1.5×10^{10}
MeCN – H_2O (9:1)	N_2	3.9×10^{10}	3.9×10^{10}	2.0×10^{10}	2.8×10^{10}
	O_2^a	4.2×10^{10}	1.2×10^{10}	6.7×10^9	6.5×10^{10}

^aCalculated from the observed pseudo-first order plot, by taking into account the concentration of oxygen dissolved.

As done in steady state experiments, the interaction of the intermediates generated by flash photolysis with different additives was investigated. Thus, addition of tetramethylethylene (TME) in the DCA/BP system quenched the transient lifetime (see Figure 4(a)). On the contrary, addition of TME to a solution of NMQ/ Ph_3P caused a noticeable decrease of the amount of the PPh_3^+ transient observed, while its lifetime remained constant (Figure 4(b)).



38 **Figure 4.(a)** Quenching of Ph_3P^+ transient generated at 510 nm in the DCA/BP system by TME.

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40 **(b)** Decrease of the end-of-pulse absorption of Ph_3P^+ transient at 380 nm by TME observed in the
41 case of NMQ; no change of the transient lifetime.
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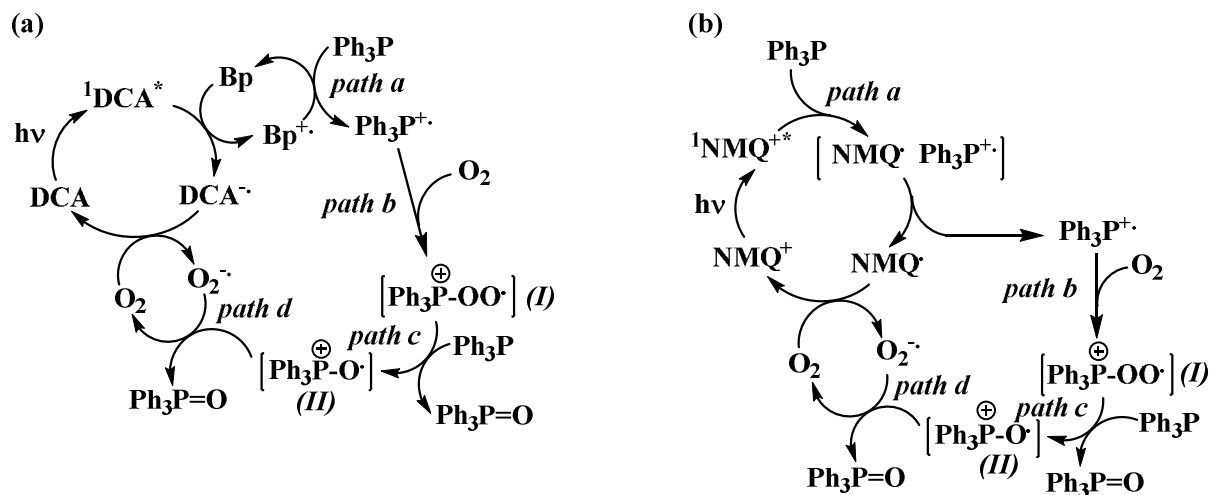
48 DISCUSSION

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51 **Photoxidation of PPh_3 via DCA/BP system and via NMQ.** As hinted above, the photoxidation of
52 triphenylphosphine by DCA is quite inefficient, but improves when using biphenyl as co-sensitizer
53 (Scheme 2, *path a*). Formation of the radical cation $\text{PPh}_3^{\cdot+}$ is clearly identified under these
54 conditions by two absorption bands located at 380 nm and 530 nm.^{16,18} The same transient was
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1 detected here when using NMQ (see Figures 2(a) and 2(b)). In both cases, the intermediate decayed
2 through a second order kinetics, reasonably attributed to back electron transfer (BET). In oxygen-
3 saturated solutions, however, trapping of photogenerated Ph_3P^+ with molecular oxygen occurred
4 and led to a pseudo-first order kinetics with both sensitizers. This behavior has been previously
5 observed under pulse radiolysis²¹ and it has been proposed that it involves formation of the peroxy
6 radical cation Ph_3PO_2^+ (Scheme 2, *path b*).^{10,18} According to Majima, reaction of this intermediate
7 with a molecule of PPh_3 and ensuing mesolytic cleavage yields triphenylphosphine oxide (Ph_3PO)
8 and radical cation Ph_3PO^+ (**II**) (Scheme 2, *path c*). Finally, intermediate (**II**) reacted with
9 superoxide ion yielding another molecule of Ph_3PO and molecular oxygen (Scheme 2, *path d*).
10 Although molecular oxygen was found to be involved in the first oxidative step, other related
11 Reactive Oxygen Species (ROS) such as singlet oxygen and superoxide ion, can be involved in the
12 overall processes. Energy transfer leading to singlet oxygen is known to proceed efficiently
13 (limiting $\Phi_\Delta = 2$ and 0.86 for DCA and NMQ, respectively)^{5e,17} but an active role of singlet oxygen
14 has been previously excluded by Majima, (for DCA/BP photocatalyzed oxidation of phosphines)¹⁶
15 and by Baciocchi for NMQ-mediated oxidation of sulfides,¹³ respectively, because the reaction is
16 faster than expected. In our case, a comparison between the bimolecular rate constant (k_t) between
17 Ph_3P and singlet oxygen reported ($1.6 \times 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$)²² and the values shown in Table 4, highlights
18 that this process does not compete efficiently with the reaction of Ph_3P^+ and molecular oxygen.
19 Furthermore, singlet oxygen photosensitization provides intermediate Ph_3PO_2 , which is a
20 phosphodioxirane intermediate²³ that is quenched by electrophilic additive Ph_2SO giving Ph_2SO_2 .
21 However, in our experimental conditions no Ph_2SO_2 was formed. Therefore, we excluded reaction
22 of singlet oxygen with Ph_3P from the reaction mechanism as a competitive oxidative pathway. On
23 the other hand, the reduced forms of both sensitizers transfer efficiently an electron to $^3\text{O}_2$
24 generating superoxide ion.¹³ The fate of this anion has been the subject of some controversy in the
25 case of sulfides, and both back electron transfer between O_2^- and R_2S^+ as well as addition reaction
26 of O_2^- with R_2S^+ have been proposed.^{9,13} The present results with phosphines, however, support
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1 none of the above paths, since addition of the ions would give the corresponding
2 phosphodioxiranes, the same intermediates involved in the singlet oxygen addition²³ that is
3 efficiently trapped by electrophiles *viz.* diphenylsulphoxide (Ph₂SO). In the experiment, addition of
4 Ph₂SO had no effect, (see Table 3), while electron acceptor 1,4-benzoquinone, a selective quencher
5 of superoxide ion, had (see Table 2). The role of superoxide ion in the photosensitization with
6 DCA/Bp or NMQ, is further evidenced by the decay traces of Ph₃P⁺ measured at 510 nm under
7 oxygen atmosphere which shows a pseudo-first order kinetics in all the solvents studied. Indeed, in
8 the case of a direct reaction of O₂⁻ with Ph₃P⁺ as the primary oxidation pathway, a second-order
9 kinetic would be observed. Therefore, coupling of superoxide ion with Ph₃P⁺ has been excluded as
10 a possible oxidation pathway from the proposed reaction mechanism. Then, O₂⁻ has a role, but does
11 not add to the phosphine radical cation. A reasonable alternative is that O₂⁻ operates as electron
12 carrier in the reduction of Ph₃PO⁺(**II**) (Scheme 2, *path d*) so that DCA⁻ and NMQ⁻ are efficiently
13 oxidized to DCA and NMQ, respectively, and therefore, the two sensitizers are not consumed
14 during the reaction. The different effect of a donor such as tetramethylethylene (TME) on NMQ and
15 DCA/BP photosensitized reaction is explained by the redox parameters of the species involved. In
16 the case of NMQ⁺, the strongly positive oxidation potential (2.70 V vs. SCE) in the excited state
17 causes competition between the phosphine (1.0 V) and the olefin (1.74 V),²⁴ resulting in a decrease
18 of the initial concentration of Ph₃P⁺ (see Figure 4b). On the other hand, with BP⁺ (E vs. SCE = 1.8
19 V) oxidation of PPh₃ is the only thermodynamically allowed reaction. However, the PPh₃⁺
20 produced was reduced by TME, resulting in an efficient quenching of the intermediate.
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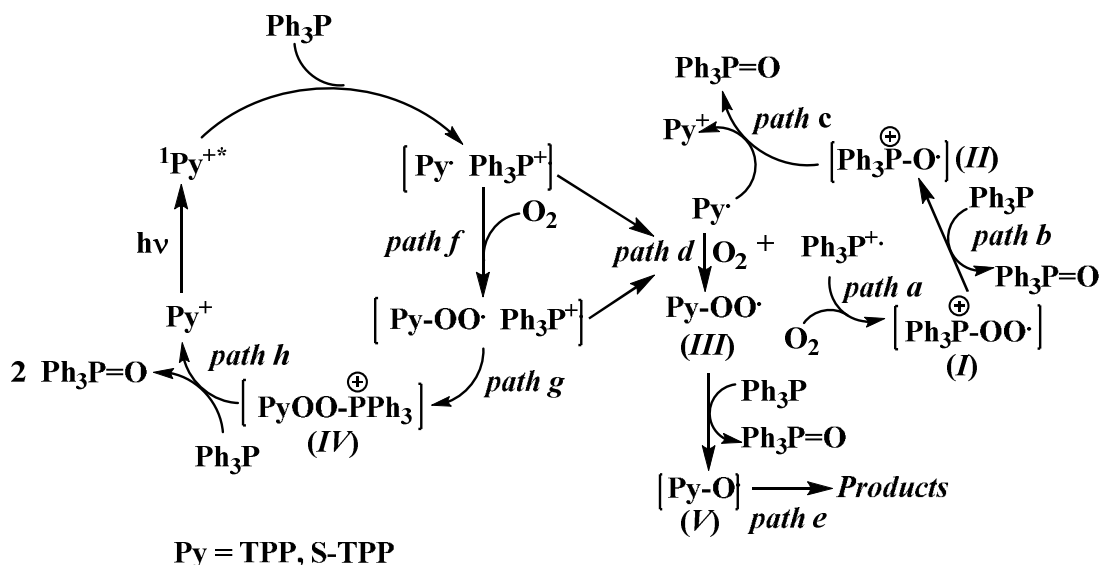
Scheme 2. Proposed mechanism for the photosensitization of triphenylphosphine with: (a) DCA/Bp system and (b) NMQ.



Photooxidation of PPh_3 via TPP and S-TPP. As in the case of the previously examined photosensitizers, electron transfer from triphenylphosphine to yield the corresponding $Ph_3P^{+•}$ was found to be the first step. The participation of both spin states of TPP and S-TPP in photooxidation reactions has been reported in the literature. The singlet excited state of TPP is involved in the photo oxidation electron transfer of different benzoic acid derivatives²⁵ whereas the participation of both TPP and S-TPP triplet excited states in electron transfer^{5e, 26} is well-known and was demonstrated in the presence of different substrates, including cinnamic acids.²⁶ In our case, the efficient quenching of the fluorescence emission by triphenyl phosphine highlighted the active role of singlet excited state of TPP. On the other hand, the S-TPP fluorescence was likewise quenched, with a quenching rate constant of $5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$. However, intersystem crossing quantum yield (0.94) largely overshadow fluorescence quantum yield (0.06) and hence, it is expected that the triplet excited state has a predominating role in the process. As observed for NMQ and the DCA/Bp system, whereas bimolecular back electron transfer is the elective pathway in nitrogen saturated solution, in the presence of oxygen the photogenerated $Ph_3P^{+•}$ reacted following a pseudo-first order decay, which highlighted again the role of molecular oxygen as the primary oxidant. Two competitive pathways have been taken into account. As proposed by Clennan in the photo oxidation

1 of sulfides,²⁷ photoinduced electron transfer resulted in the formation of a radical/radical ion
2 intimate pair. We suggested that bimolecular reaction with ³O₂ occurs either at this stage or after
3 solvation, depending on ion solvating power of the solvent. In the case of polar solvents (MeCN,
4 MeOH and MeCN/H₂O mixture), reaction of solvated PPh₃⁺ with ³O₂ afforded the oxygenated
5 intermediate Ph₃POO⁺ (**I**) (Scheme 3, *path a*), which was previously proposed for DCA/Bp and
6 NMQ sensitization. As hinted above, intermediate **I** reacts with Ph₃P to produce a Ph₃PO molecule
7 and the radical cation PPh₃O^{•+} (**II**) and then, the last intermediate oxidizes TPP[•] radical regenerating
8 the sensitizer TPP⁺ (Scheme 3, *paths b* and *c*). On the other hand, addition of ³O₂ to the reduced
9 (thia)pyrylium radical (TPP[•] or S-TPP[•]) affords the peroxy radical TPP-OO[•] (**III**), and this in turn
10 reacts with PPh₃ to produce the triphenylphosphine oxide (Scheme 3, *path d*). This has analogy with
11 the observed oxygen transfer to aromatic and aliphatic sulfides by radicals of this type, for example,
12 the cumoylperoxy radical or halogenated peroxy radicals.²⁸ Thus, reaction via a TPP-OO[•] radical is
13 a possibility, but in such a case oxygen transfer involves consumption of the sensitizer, since the
14 alkoxy radicals (**V**) resulting from oxygen transfer (TPP-OO[•] + PPh₃ → TPP-O[•] + Ph₃PO; Scheme 3,
15 *path e*) would further react with irreversible degradation of the pyrylium ring. In fact, electron
16 transfer from water that has an oxidation potential (E = 1.28 V) comparable to that of PPh₃ and thus
17 a further oxidizing species, hydroxyl radical, is formed and increases the reaction efficiency.²⁹
18 Intermediate (**III**) or any other oxidizing species may contribute to the oxidation of Ph₃P as a side
19 pathway (Ph₃PO is formed quantitatively while the consumption of the sensitizers take place in a
20 few percent). Previous work by Clennan using sulfides as probes showed that these sensitizers did
21 not form neither singlet oxygen nor superoxide ($\Delta G_{ET} < 10 \text{ kcal mol}^{-1}$).²⁷ Thus, the cyclic inner
22 sphere mechanism shown in Scheme 3, viz. *paths f, g* and *h*, is the exclusive path in aprotic
23 solvents, while formation of radicals occurs in polar and protic media. The exclusive presence of **III**
24 in polar solvents is also evidenced by the addition of quencher BQ. In fact, the reaction rate is only
25 diminished in polar and protic solvent in the presence of BQ, whereas no effect was measured in
26 dichloromethane.

Scheme 3. Reaction mechanism for the photosensitization of triphenylphosphine with TPP and S-TPP.



Finally, addition of biphenyl is required when DCA is the sensitizer, but an increase of rate in the presence of biphenyl is observed for all of the examined photocatalysts (see Figure 1(b)). Thus, BP is an efficient co-oxidant, and the improvement depends on the oxidation potential of the sensitizer used. The effect is largest when NMQ is used (up to six times the initial rate).

CONCLUSIONS.

The photosensitized oxidation reactions examined in the present paper take place, at least, through two different reaction mechanisms, depending both on the nature of the photosensitizer employed and on the solvent used. The first step is in every case an electron-transfer process from the electron donor (triphenyl phosphine) to the photoexcited sensitizer providing a triphenylphosphine radical cation, as confirmed by both preparative photochemical experiments and laser flash photolysis analyses. In the case of photosensitization with DCA/Bp system and NMQ, respectively, the Ph_3P radical-cation then reacts with molecular oxygen ($^3\text{O}_2$) following a pseudo-first order kinetics and affording the oxygenated intermediate $\text{Ph}_3\text{P}^+\text{OO}^\cdot$ (I). Then, such a transient reacts with Ph_3P to

1 afford $\text{Ph}_3\text{P}=\text{O}$ and intermediate Ph_3PO^+ (**II**). Superoxide ion ($\text{O}_2^{\cdot-}$) is also generated during the
2 irradiation and operates as electron carrier in the reduction of Ph_3PO^+ (**II**) to $\text{Ph}_3\text{P}=\text{O}$, thus no
3 sensitizers consumption is observed during the reaction. Formation of Ph_3PO^+ (**II**) can be observed
4 also in the case of cationic photosensitizers (TPP and S-TPP) in polar solvents, where molecular
5 oxygen plays again the role of the primary oxidant. On the other hand, in apolar media, a cyclic
6 inner sphere mechanism is the exclusive path that provides triphenylphosphine oxide via the
7 formation of a peroxidic intermediate (**IV**) and the subsequent consumption of the sensitizer.
8 Finally, the finding that triphenylphosphine radical cation reacts efficiently with molecular oxygen
9 sheds some light on the reactivity of triarylphosphines under photosensitization conditions.
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22 EXPERIMENTAL DETAILS

23 **Materials** .Compounds triphenylphosphine, triphenylphosphine oxide, diphenyl sulfoxide, 1,4-
24 dimethoxybenzene, benzoquinone, tetramethylethylene, biphenyl and the photocatalyst 2,4,6-
25 triphenylpyrylium tetrafluoroborate (TPP) were commercially available and used as received. TPP
26 was washed with water and dried before use to eliminate traces of acids. DCA,³⁰ *N*-
27 methylquinolinium tetrafluoroborate³¹ and 2,4,6-triphenylthiapyrylium tetrafluoroborate (S-TPP)³²
28 were prepared by published procedures. All the solvents used were of spectroscopic grade and used
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40 **Photochemical reactions.** The photooxidations were carried out by using 0.01– 0.1 M solutions (2
41 mL) of the triphenylphosphine in the presence of DCA, NMQ, S-TPP, or TPP (5×10^{-4} to 1×10^{-3} M)
42 in acetonitrile, methanol, 1,2-dichloroethane and acetonitrile water (9:1). The solutions were
43 contained in rubber-stoppered Pyrex tubes (1 cm diameter) and exposed to four phosphor-coated 15
44 W lamps with emission centered at 400 nm (for DCA, S-TPP and TPP) or 366 nm (for NMQ) while
45 a stream of dry oxygen saturated with the appropriate solvent was passed into the solution through a
46 needle. The products were determined by means of GC analyses on the basis of calibration curves
47 in the presence of cyclododecane as internal standard and by HPLC analyses. Experiments for
48 quantum yield determination were limited to $\geq 10\%$ conversion and the DCA-sensitized oxidation of
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1,1 diphenylethene ($\Phi_{-1} = 0.8$) was used as actinometer to measure the quantum yields.³³ These experiments were performed with an optical bench provided with a high pressure Hg lamp and the appropriate interference filters. Irradiation of such solutions with photosensitizers DCA, TPP and S-TPP were carried out with a filter centered at 405 nm, while for the case of NMQ the filter was centered at 366 nm. The samples were placed in quartz cells (10 × 10 mm) while a stream of dry oxygen saturated with the appropriate solvent was passed into the solution through a needle. Experiments at a higher conversion (>50%) were also carried out, and no significant difference in the product distribution was noted. A solution of TPP in MeOH was appreciably bleached and the addition of further amounts of the sensitizer was required in order to continue the oxidation. In order to exclude any contribution by spurious light to the photooxidation of triphenyl phosphine, all the irradiations were performed in a dark room and inside of a laboratory hoodboard where the temperature was between 20 – 22 °C.

Steady-State Fluorescence Quenching. Solutions of the photosensitizers in MeCN were placed in a quartz cell (10 × 10 mm section) at a concentration adjusted to obtain an A value of 0.5 at the maximum emission wavelength characteristic of each photosensitizer. The fluorescent spectra were recorded with a fluorimeter. The quenching rate constants (k_Q) were obtained using the Stern-Volmer method applying least-square linear regression fitting procedure and the r^2 values were used to judge the goodness of fit.

Time-resolved laser flash spectroscopy. Nano-to-microsecond transient absorption experiments were performed using a nanosecond laser flash photolysis apparatus equipped with a 20 Hz Nd:YAG laser (20 ns, 1 mJ at 355 nm) and a 150 W Xe flash lamp as the probe light. Samples were placed in a quartz cell (10 × 10 mm section) at a concentration adjusted to obtain an OD value of 1.0 at 355 nm. Furthermore, the samples were flushed with a stream of either argon or oxygen during 20 minutes in order to create an inert and an oxidative atmosphere, respectively. Least-squares linear regression fittings were carried out in order to judge the goodness of the fit with the correlation coefficients (square root) better than 0.99. Mono-exponential fittings procedures were

1 carried out and the quality of the data obtained was judged from the χ^2 parameter and distribution of
2 the residuals. All of the laser flash photolysis experiments were carried out at 20 °C. Quenching of
3 the Ph_3P^+ transient by TME were performed with the same apparatus using the Stern-Volmer
4 method.
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10 11 12 13 **ACKNOWLEDGMENTS.**

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