Reactive Oxygen Species (ROS)-vs Peroxyl-Mediated Photosensitized Oxidation of Triphenylphosphine: A Comparative Study

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ABSTRACT: The oxidation of triphenylphosphine in the presence of various photocatalytic systems (dicyanoanthracene/biphenyl, N-methylquinolinium, triphenylpyrylium, and thiatriphenylpyrylium tetrafluoroborate) 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 azide) 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.
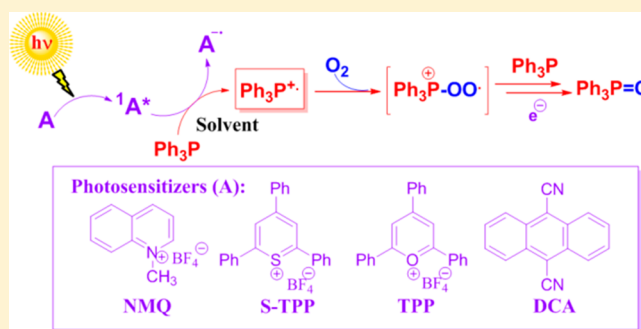
INTRODUCTION

Molecular oxygen ($^3O_2$) 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 ($^3O_2$) 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 photocatalysis[2] or by using a suitable photocatalyst to produce singlet oxygen ($^1O_2$) via sensitization in a spin-allowed process[3] 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 offer 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] quinolinium,[6] and acridinium salts[7]) 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, $E_{ox}(Ar_3P/Ar_3P^{+\cdot})$ = 1.00 V][10] and are of interest as excellent electron donors. The radical cation then evolved to a stable photoproduct, the phosphine oxide ($Ar_3P=O$). This intermediate

exhibits a dual reactivity, as an electrophile (in the presence of different nucleophiles such as alcohols, water, halides, hydroxyl anions, and bases[11]) 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 photo-oxidation 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 these photocatalysts oxidation of triphenylphosphine is in every case an exergonic process (ΔG = −22.4 kcal mol^{-1} for DCA; −62.3 kcal mol^{-1} for NMQ; −48.4 kcal mol^{-1} for TPP and −48.2 kcal mol^{-1} for S-TPP). In the case of DCA, the use of biphenyl as cosensitizer was used to improve the process, as previously observed by Majima and co-workers.[16]
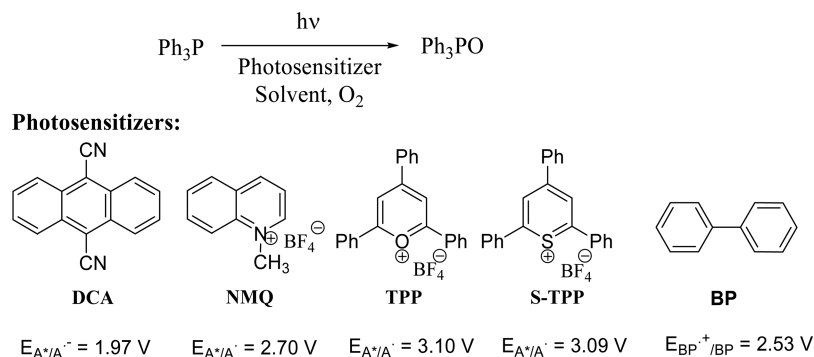
RESULTS

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

Scheme 1. Photosensitized Oxidation Reaction of Triphenylphosphine and Chemical Structures of the Photosensitizers

$$Ph_3P \xrightarrow[\text{Photosensitizer Solvent, O}_2]{h\nu} Ph_3PO$$

Photosensitizers:

DCA	NMQ	TPP	S-TPP	BP
$E_{A^*/A^{\cdot-}}$ = 1.97 V	$E_{A^*/A^{\cdot}}$ = 2.70 V	$E_{A^*/A^{\cdot}}$ = 3.10 V	$E_{A^*/A^{\cdot}}$ = 3.09 V	$E_{BP^{\cdot+}/BP}$ = 2.53 V

significantly lower emission (Φ_F = 0.06). In every case, the fluorescence quenching by triphenylphosphine occurred efficiently (k_q ranging from 1.9 to 7.9 × 10^{10} M^{-1} 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$_3$P in MeCN

photosensitizer	$\Phi_F{}^a$	τ/ ns	k_q/M^{-1} 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$_3$P 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$_3$P and Ph$_3$PO 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 λ = 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$_2$SO)) 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.

Photocatalyzed Oxidation via DCA. Consistent with what was observed in previous reports,[5e,17] the DCA/biphenyl photosensitized oxidation of Ph$_3$P was found to be quite inefficient (Φ < 0.05). The use of a protic environment further lowered the reaction efficiency (from Φ = 0.033 to 0.015 when moving from neat acetonitrile to methanol). The oxidation rate was not unaffected by the presence of 1,4-dimethoxybenzene (DMB), whereas the quenching effect of diphenylsulfoxide (Ph$_2$SO) was found to be significant only in dichloromethane solution, where the oxidation rate decreased from 2.88 to 1.10 μmol min^{-1}. The addition of 1,4-benzoquinone reduced the rate value of ca. one-third in all of the systems tested.

Table 2. Quantum Yield of Consumption of Ph$_3$P 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] [Ph$_3$P]: 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^{-2} M as cosensitizer). [c] λ_{exc}: 365 nm. All data were obtained with a ± 0.001 error

Photocatalyzed Reactions via NMQ. With NMQ as the photosensitizer, the oxidation quantum yields improved, with maximal values in polar aprotic solvents (up to 0.169 in dichloromethane). In the absence of oxygen, the photo oxidation rate was decreased to one tenth of the initial value. Again, the use of a protic medium resulted in a lowering of the quantum yield value. As for quenchers, DMB and Ph$_2$SO had little or no effect on the rate of phosphine oxide formation, while the use of BQ generally led to a significant decrease of the rate value, as previously observed with DCA.

Photocatalyzed Reactions via TPP and S-TPP. With the heterocyclic salts TPP and S-TPP as the photocatalysts the oxidation quantum yield varied from 2 to 9% with the former (maximal value in methanol and in dichloromethane) and from 9 to 26.5% with the latter (maximal value in acetonitrile−water 9:1). None of the above additives caused a large effect, with some slowing down of the reaction only with BQ in the oxidation in polar solvents.

However, these photocatalysts were partially consumed during the irradiation in oxygen saturated nucleophilic media, such as MeOH, MeCN, and aqueous MeCN solutions of the phosphine (see an example in Figure 1a). The formation of Ph$_3$PO remained quantitative, though. In fact, photosensitization of Ph$_3$P with TPP in O$_2$-saturated MeCN−H$_2$O (9:1) at 405 nm on an optical bench provides 95% yield of Ph$_3$PO at a fixed reaction time while TPP is only consumed in 23% yield. Likewise, with S-TPP Ph$_3$PO is formed in 92% yield while S-TPP in consumed in only 3% yield. Finally, no significant consumption of both TPP and S-TPP was observed in apolar solvents.

The use of biphenyl as a co-oxidant of all of the examined catalysts has been also considered. Interestingly, an enhancement of the photo oxidation rate has been observed with all of

Table 3. Rate of Ph$_3$PO [μmol·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

[a]Amounts of triphenylphosphineoxide formed in μmol·min^{-1}. [b]5 × 10^{-2} M 1,4-dimethoxybenzene (DMB). [c]1.25 × 10^{-3} M 1,4-Benzoquinone (BQ). [d]2.5 × 10^{-3} M Ph$_2$SO.
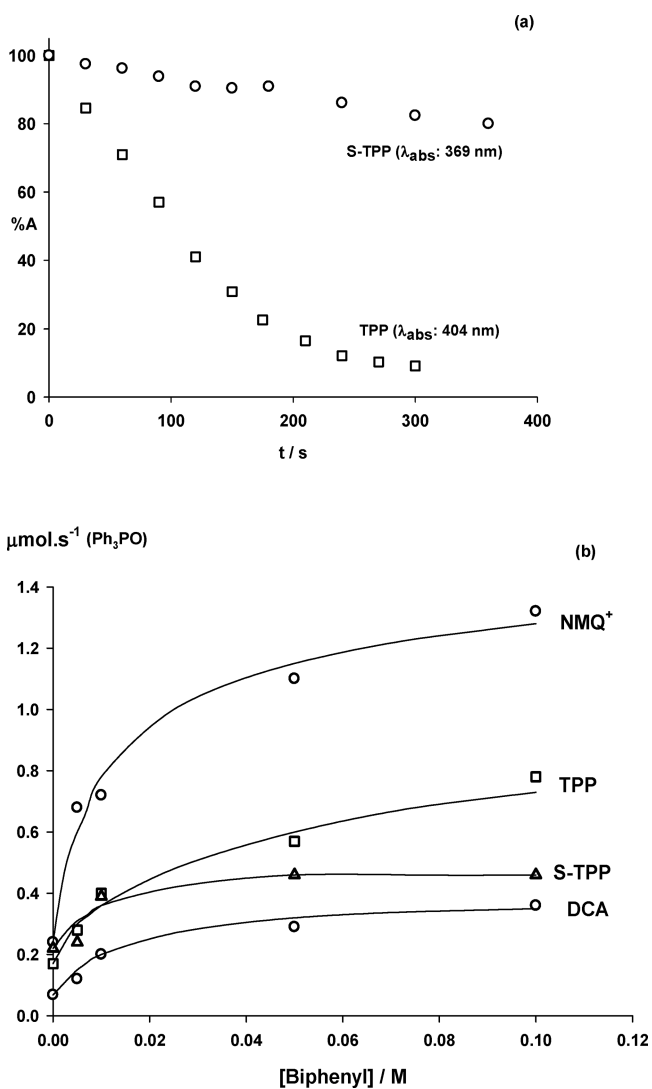

Figure 1. (a) Relative consumption of photosensitizers TPP and S-TPP during irradiation with λ_{exc}: 405 nm of O$_2$-saturated solutions of PPh$_3$ (0.010 M) in MeCN − H$_2$O (9:1). (b) Effect of addition of biphenyl on the photosensitized oxidation of O$_2$-saturated acetonitrile solution of PPh$_3$ (0.010 M).

the photosensitizers used, with a maximum increase in the case of NMQ, for which the oxidation rate increased by a factor of 5 (Figure 1b).

Time-Resolved Spectroscopic Measurements. The steady state irradiations have been supplemented by laser flash photolysis experiments. The spectra obtained in the

DCA/biphenyl system in the presence of PPh$_3$ clearly show the formation of three different absorption bands located at 530, 600, and 730 nm (Figure 2a). In accord with the literature[18] we assigned the last two bands to the biphenyl radical cation (BP·$^+$) and DCA·$^-$, respectively. Similar results were obtained with the other photocatalysts in all of the chosen media. In all of the cases studied, formation of the two absorption bands located at 380 and 530 nm was observed but, due to the interference of other intermediates involved, only the former band was clearly visible in the presence of NMQ (Figure 2b). Experiments in the presence of sodium azide showed that both absorption bands were quenched by azide anion with similar k_q values (k_q = 2.4−2.8 × 10^8 M^{-1} s^{-1}). Therefore, these bands can be univocally assigned to the absorption spectrum of a single transient, the triphenylphosphine radical cation (PPh$_3$·$^+$). Likewise, the reduced forms of the photo-oxidants (the corresponding N-methylquinolyl, pyryl, and thiapyryl radicals) were also detected along with the transient radical cation. Representative examples are shown in Figure 2 for MeCN.

The transient Ph$_3$P·$^+$ was found to decay with a second-order rate constant (k_2) of 10^9−10^{10} M^{-1} s^{-1} (see Table 4) in N$_2$-saturated solution, whereas in O$_2$-saturated solution a pseudo-first-order decay was observed. In the latter case, a second-order rate constant of 10^9−10^{10} M^{-1} s^{-1} was calculated by considering the concentration of O$_2$ solubilized in each of the solvents used. Representative decay curves of transient PPh$_3^+$· in N$_2$- and O$_2$-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 Ph$_3$P/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.

As done in steady state experiments, the interaction of the intermediates generated by flash photolysis with different additives was investigated. Thus, addition of tetramethyl-ethylene (TME) in the DCA/BP system quenched the transient lifetime (see Figure 4a). On the contrary, addition of TME to a solution of NMQ/Ph$_3$P caused a noticeable decrease of the amount of the PPh$_3^+$· transient observed, while its lifetime remained constant (Figure 4b).

■ DISCUSSION

Photoxidation of PPh$_3$ via DCA/BP System and via NMQ. As hinted above, the photoxidation of triphenylphos-phine by DCA is quite inefficient, but improves when using biphenyl as cosensitizer (Scheme 2, path a). Formation of the radical cation PPh$_3$·$^+$ is clearly identified under these conditions
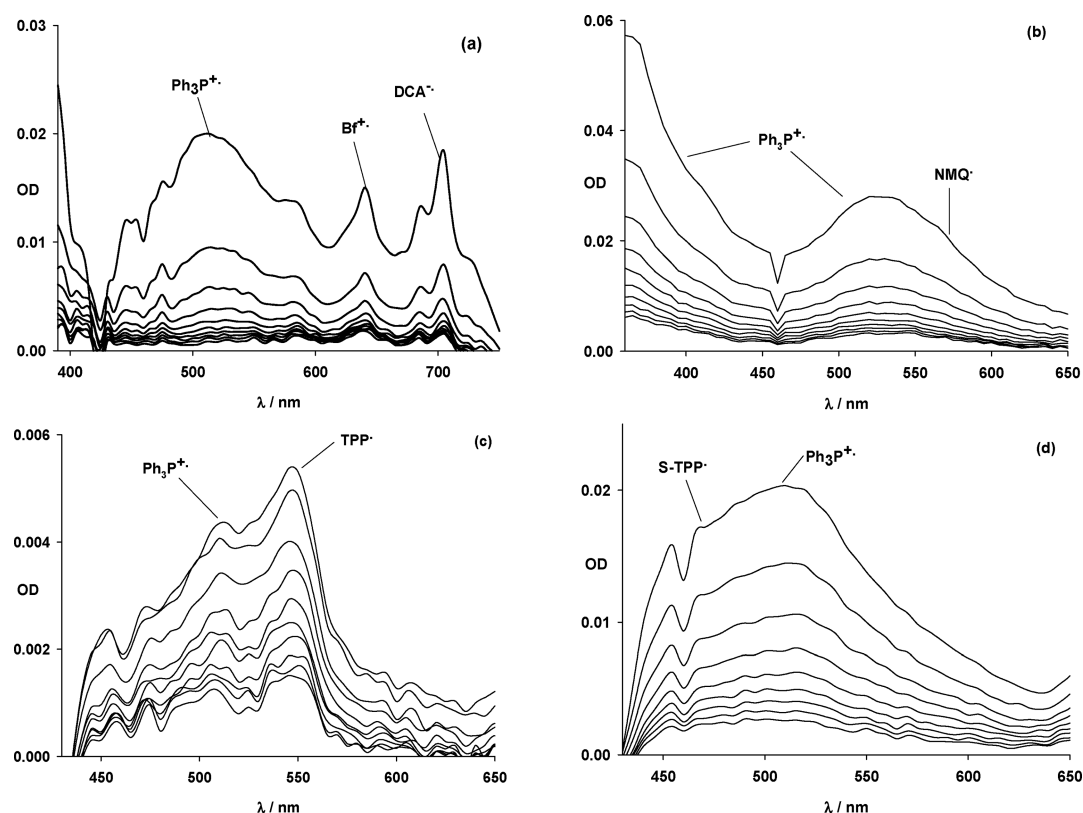
Figure 2. Transients absorption spectra recorded after a laser pulse (10 μs, λ_{exc}: 355 nm) of N_2-saturated acetonitrile solution of PPh_3 (0.0110 M) in the presence of: (a) DCA and BP; (b) NMQ; (c) TPP; and (d) S-TPP.

Table 4. Second-Order Decay Parameters of $Ph_3P^{+\cdot}$ Sensitized by DCA, TPP, S-TPP, and NMQ in N_2- and O_2-Saturated Organic Solvents

		$k_2/M^{-1}\cdot s^{-1}$			
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}

^{a}Calculated from the observed pseudo-first order plot, by taking into account the concentration of oxygen dissolved.

by two absorption bands located at 380 and 530 nm.[16,18] The same transient was detected here when using NMQ (see Figure 2a and b). In both cases, the intermediate decayed through a second order kinetics, reasonably attributed to back electron transfer (BET). In oxygen-saturated solutions, however, trapping of photogenerated $Ph_3P^{\cdot+}$ with molecular oxygen occurred and led to a pseudo-first order kinetics with both sensitizers. This behavior has been previously observed under pulse radiolysis[21] and it has been proposed that it involves formation of the peroxyl radical cation $Ph_3PO_2^{\cdot+}$ (Scheme 2, path b).[10,18] According to Majima, reaction of this intermediate with a molecule of PPh_3 and ensuing mesolytic cleavage yields triphenylphosphine oxide (Ph_3PO) and radical cation $Ph_3PO^{\cdot+}$ (**II**) (Scheme 2, path c). Finally, intermediate (**II**) reacted with superoxide ion yielding another molecule of Ph_3PO and molecular oxygen (Scheme 2, path d). Although molecular oxygen was found to be involved in the

first oxidative step, other related ROS, such as singlet oxygen and superoxide ion, can be involved in the overall processes. Energy transfer leading to singlet oxygen is known to proceed efficiently (limiting Φ_Δ = 2 and 0.86 for DCA and NMQ, respectively)[5e,17] but an active role of singlet oxygen has been previously excluded by Majima (for DCA/BP photocatalyzed oxidation of phosphines),[16] and by Baciocchi for NMQ-mediated oxidation of sulfides,[13] respectively, because the reaction is faster than expected. In our case, a comparison between the bimolecular rate constant (k_r) between Ph_3P and singlet oxygen reported (1.6×10^7 $M^{-1}\cdot s^{-1}$)[22] and the values shown in Table 4, highlight that this process does not compete efficiently with the reaction of $Ph_3P^{\cdot+}$ and molecular oxygen. Furthermore, singlet oxygen photosensitization provides phosphodioxirane intermediates Ph_3PO_2[23] that is quenched by electrophilic additive Ph_2SO giving Ph_2SO_2. However, in our experimental conditions no Ph_2SO_2 was formed. Therefore, we
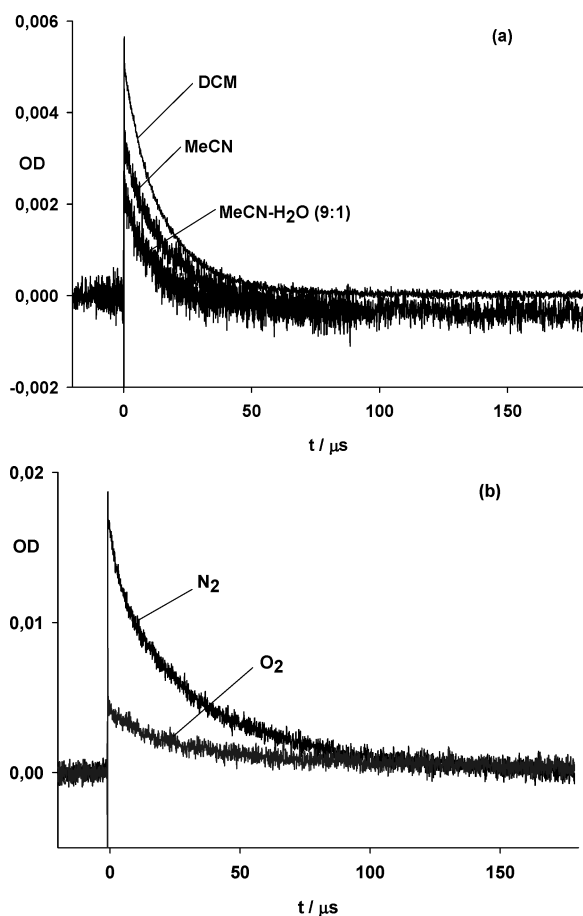
Figure 3. (a) Decay traces of $PPh_3^+\cdot$ after a laser pulse (λ_{exc}: 355 nm) of N_2-saturated solutions of PPh_3 (0.010 mol.dm^{-3}) and NMQ (1.0 × 10^{-4} mol dm^{-3}) in dichloromethane, MeCN, and MeCN-H$_2$O 9:1 mixture recorded at 510 nm. (b) Decay traces of $PPh_3^+\cdot$ after a laser pulse (λ_{exc}: 355 nm) of N_2- and O_2-saturated acetonitrile solutions of PPh_3 (0.010 mol dm^{-3}) and S-TPP (1.0 × 10^{-4} mol dm^{-3}) recorded at 510 nm.
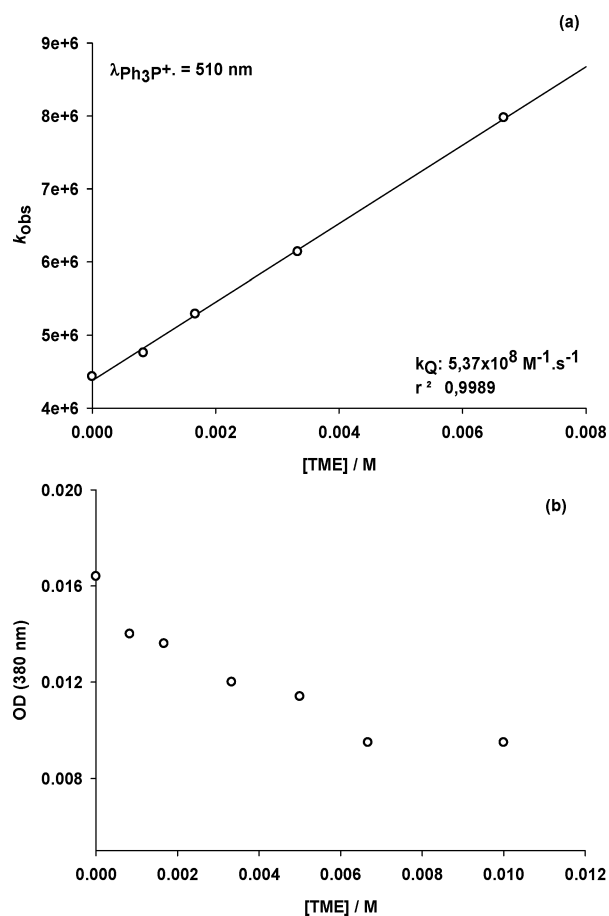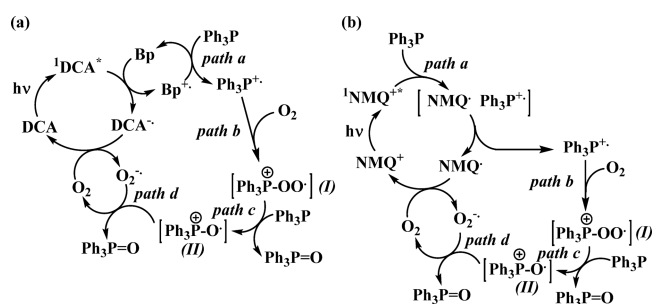
Figure 4. (a) Quenching of $Ph_3P^+\cdot$ transient generated at 510 nm in the DCA/BP system by TME. (b) Decrease of the end-of-pulse absorption of $Ph_3P^+\cdot$ transient at 380 nm by TME observed in the case of NMQ; no change of the transient lifetime.

Scheme 2. Proposed Mechanism for the Photosensitization of Triphenylphosphine with (a) DCA/Bp System and (b) NMQ
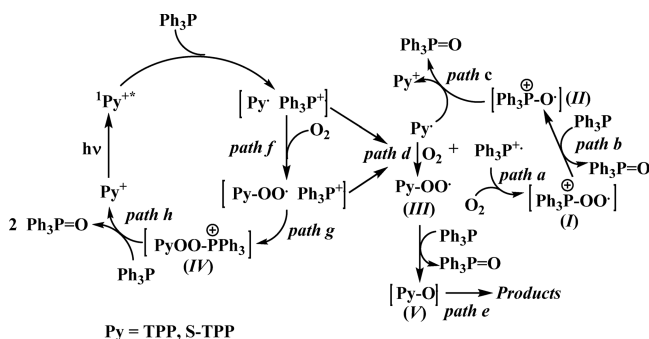

excluded reaction of singlet oxygen with Ph_3P from the reaction mechanism as a competitive oxidative pathway. On the other hand, the reduced forms of both sensitizers transfer efficiently an electron to $^3O_2$ generating superoxide ion.[13] The fate of this anion has been the subject of some controversy in the case of sulfides, and both back electron transfer between $O_2\cdot^-$ and $R_2S\cdot^+$ as well as addition reaction of $O_2\cdot^-$ with $R_2S\cdot^+$ have been proposed.[9,13] The present results with phosphines, however, support none of the above paths, since addition of the ions would give the corresponding phosphodioxiranes, the same intermediates involved in the singlet oxygen addition[23] that is efficiently trapped by electrophiles viz. diphenylsulfoxide (Ph_2SO). In the experiment, addition of Ph_2SO had no effect, (see Table 3), while electron acceptor 1,4-benzoquinone, a selective quencher of superoxide ion, had an effect (see Table 2). The role of superoxide ion in the photosensitization with DCA/Bp or NMQ is further evidenced by the decay traces of $Ph_3P\cdot^+$ measured at 510 nm under oxygen atmosphere which shows a pseudo-first order kinetics in all the solvents studied. Indeed, in the case of a direct reaction of $O_2\cdot^-$ with $Ph_3P\cdot^+$ as the primary oxidation pathway, a second-order kinetic would be observed. Therefore, coupling of superoxide ion with $Ph_3P\cdot^+$ has been excluded as a possible oxidation pathway from the proposed reaction mechanism. Then, $O_2\cdot^-$ has a role, but does

not add to the phosphine radical cation. A reasonable alternative is that $O_2\cdot^-$ operates as electron carrier in the reduction of $Ph_3PO\cdot^+$ (**II**) (Scheme 2, path d) so that DCA$\cdot^-$ and NMQ$\cdot$ are efficiently oxidized to DCA and NMQ, respectively, and therefore, the two sensitizers are not consumed during the reaction. The different effect of a donor, such as tetramethylethylene (TME) on NMQ and DCA/BP photosensitized reaction, is explained by the redox parameters of the species involved. In the case of NMQ$^+$, the strongly positive oxidation potential (2.70 V vs SCE) in the excited state causes competition between the phosphine (1.0 V) and the olefin (1.74 V),[24] resulting in a decrease of the

initial concentration of Ph₃P·⁺ (see Figure 4b). On the other hand, with BP·⁺ (E vs SCE = 1.8 V) oxidation of PPh₃ is the only thermodynamically allowed reaction. However, the PPh₃·⁺ produced was reduced by TME, resulting in an efficient quenching of the intermediate.

Photoxidation of PPh₃ via TPP and S-TPP. As in the case of the previously examined photosensitizers, electron transfer from triphenylphosphine to yield the corresponding Ph₃P⁺· 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 derivatives[25] 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 × 10¹⁰ M⁻¹ 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 Ph₃P·⁺ 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 of sulfides,[27] photoinduced electron transfer resulted in the formation of a radical/radical ion intimate pair. We suggested that bimolecular reaction with ³O₂ occurs either at this stage or after solvation, depending on ion solvating power of the solvent. In the case of polar solvents (MeCN, MeOH, and MeCN/H₂O mixture), reaction of solvated PPh₃⁺· with ³O₂ afforded the oxygenated intermediate Ph₃POO⁺· (**I**) (Scheme 3, path a), which was previously proposed for

Scheme 3. Reaction Mechanism for the Photosensitization of Triphenylphosphine with TPP and S-TPP

aromatic and aliphatic sulfides by radicals of this type, for example, the cumoylperoxyl radical or halogenated peroxyl radicals.[28] Thus, reaction via a TPP-OO· radical is a possibility, but in such a case oxygen transfer involves consumption of the sensitizer, since the alkoxyl radicals (**V**) resulting from oxygen transfer (TPP-OO· + PPh₃ → TPP-O· + Ph₃PO; Scheme 3, path e) would further react with irreversible degradation of the pyrylium ring. In fact, electron transfer from water that has an oxidation potential (E = 1.28 V) comparable to that of PPh₃ and thus a further oxidizing species, hydroxyl radical, is formed and increases the reaction efficiency.[29] Intermediate (**III**) or any other oxidizing species may contribute to the oxidation of Ph₃P as a side pathway (Ph₃PO is formed quantitatively while the consumption of the sensitizers take place in a few percent). Previous work by Clennan using sulfides as probes showed that these sensitizers did not form neither singlet oxygen nor superoxide (ΔG_{ET} < 10 kcal mol⁻¹).[27] Thus, the cyclic inner sphere mechanism shown in Scheme 3, viz. paths f, g, and h, is the exclusive path in aprotic solvents, while formation of radicals occurs in polar and protic media. The exclusive presence of **III** in polar solvents is also evidenced by the addition of quencher BQ. In fact, the reaction rate is only diminished in polar and protic solvent in the presence of BQ, whereas no effect was measured in dichloromethane.

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 1b). 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 Ph₃P radical-cation then reacts with molecular oxygen (³O₂) following a pseudo-first order kinetics and affording the oxygenated intermediate Ph₃POO·⁺ (**I**). Then, such a transient reacts with Ph₃P to afford Ph₃P═O and intermediate Ph₃PO·⁺ (**II**). Superoxide ion (O₂·⁻) is also generated during the irradiation and operates as electron carrier in the reduction of Ph₃PO·⁺(**II**) to Ph₃P═O, thus no sensitizers consumption is observed during the reaction. Formation of Ph₃PO·⁺(**II**) can be observed also in the case of cationic photosensitizers (TPP and S-TPP) in polar solvents, where molecular oxygen plays again the role of the primary oxidant. On the other hand, in apolar media, a cyclic inner sphere mechanism is the exclusive path that provides triphenylphosphine oxide via the formation of a peroxidic intermediate (**IV**) and the subsequent consumption of the sensitizer. Finally, the finding that triphenylphosphine radical cation reacts efficiently with molecular oxygen sheds some light on the reactivity of triarylphosphines under photosensitization conditions.

DCA/Bp and NMQ sensitization. As hinted above, intermediate **I** reacts with Ph₃P to produce a Ph₃PO molecule and the radical cation PPh₃O·⁺· (**II**) and then, the last intermediate oxidizes TPP· radical regenerating the sensitizer TPP⁺ (Scheme 3, paths b and c). On the other hand, addition of ³O₂ to the reduced (thia)pyrylium radical (TPP· or S-TPP·) affords the peroxyl radical TPP-OO· (**III**), and this in turn reacts with PPh₃ to produce the triphenylphosphine oxide (Scheme 3, path d). This has analogy with the observed oxygen transfer to

EXPERIMENTAL DETAILS

Materials. Compounds triphenylphosphine, triphenylphosphine oxide, diphenyl sulfoxide, 1,4-dimethoxybenzene, benzoquinone, tetramethylethylene, biphenyl, and the photocatalyst 2,4,6-triphenyl-pyrylium tetrafluoroborate (TPP) were commercially available and used as received. TPP was washed with water and dried before use to eliminate traces of acids. DCA,[30] N-methylquinolinium tetrafluoroborate,[31] and 2,4,6-triphenylthiapyrylium tetrafluoroborate (S-TPP)[32] were prepared by published procedures. All the solvents used were of spectroscopic grade and used as received.

Photochemical Reactions. The photooxidations were carried out by using 0.01−0.1 M solutions (2 mL) of the triphenylphosphine in the presence of DCA, NMQ, S-TPP, or TPP (5×10^{-4} to 1×10^{-3} M) in acetonitrile, methanol, 1,2-dichloroethane, and acetonitrile water (9:1). The solutions were contained in rubber-stoppered Pyrex tubes (1 cm diameter) and exposed to four phosphor-coated 15 W lamps with emission centered at 400 nm (for DCA, S-TPP, and TPP) or 366 nm (for NMQ) while a stream of dry oxygen saturated with the appropriate solvent was passed into the solution through a needle. The products were determined by means of GC analyses on the basis of calibration curves in the presence of cyclododecane as internal standard and by HPLC analyses. Experiments for quantum yield determination were limited to ≥10% conversion and the DCA-sensitized oxidation of 1,1 diphenylethene ($\Phi_{-1} = 0.8$) was used as actinometer to measure the quantum yields.[33] These experiments were performed by using 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-squares linear regression fitting procedure and the r^2 values were used to judge the goodness of fit.

Time-Resolved Laser Flash Spectroscopy. Nano to micro 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 min 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. Monoexponential fittings procedures were carried out and the quality of the data obtained was judged from the χ^2 parameter and distribution of the residuals. All of the laser flash photolysis experiments were carried out at 20 °C. Quenching of the $Ph_3P^{+\cdot}$ transient by TME were performed with the same apparatus using the Stern−Volmer method.

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Notes

The authors declare no competing financial interest.

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