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The Role of Structural Effects on the Reactions of Alkoxyl Radicals with Trialkyl and Triaryl Phosphites. A Time-Resolved Kinetic Study

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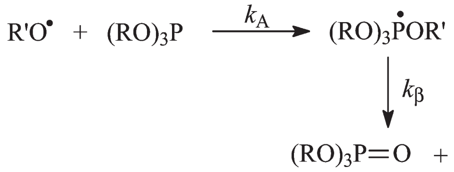
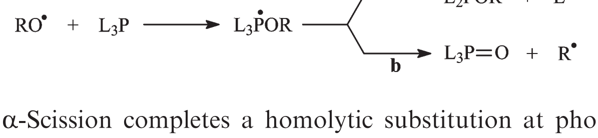


A time-resolved kinetic study on the reactions of alkoxyl radicals with trialkyl and triaryl phosphites ($(RO)_3P$: R = Me, Et, *i*-Pr, *t*-Bu; $(ArO)_3P$: Ar = C_6H_5, 2,4-(t-Bu)$_2C_6H_3$) has been carried out. In the $(RO)_3P$ series, the alkoxyl radicals (cumyloxyl ($CumO^\bullet$) and benzyloxyl ($BnO^\bullet$)) undergo addition to the phosphorus center with formation of intermediate tetraalkoxyphosphoranyl radicals ($R'OP^\bullet(OR)_3$: R = Me, Et, *i*-Pr, *t*-Bu; R′ = Bn, Cum). The addition rate constants are influenced by steric effects, decreasing on going from R = Me to R = *t*-Bu and from $BnO^\bullet$ to $CumO^\bullet$. Rate constants for β-scission of the phosphoranyl radicals $R'OP^\bullet(OR)_3$ have also been determined, increasing, for a given alkyl group R, in the order R′ = *tert*-butyl < R′ = benzyl < R′ = cumyl and, for a given R′ group, on going from R = Me to R = *i*-Pr. This behavior has been explained in terms of the relative stability of the radicals formed after β-scission, suggesting moreover that steric effects play in this case a minor role. $CumO^\bullet$ reacts with triaryl phosphites $(ArO)_3P$ to give phenoxyl radicals, with rate constants that are influenced to a limited extent by substitution of the aromatic rings. The radical scavenging ability of these substrates is briefly discussed.

Introduction

The reactions of alkoxyl radicals ($RO^\bullet$) with trivalent organophosphorus compounds (L_3P) have attracted considerable interest.[1−6] The radical adds to the phosphorus center affording phosphoranyl radicals ($L_3P^\bullet OR$) that, depending on their structure, can fragment following two main pathways: α-scission with cleavage of a P−L bond (Scheme 1, path a) and β-scission involving the cleavage of the O−R bond (Scheme 1, path b).

SCHEME 1



α-Scission completes a homolytic substitution at phosphorus, and the process may be concerted depending on the stability of the displaced radical.[2,7] β-Scission results instead in the overall oxidation from phosphorus(III) to phosphorus(V) and provides in particular a convenient method for the deoxygenation of alkoxyl radicals.

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The factors governing the formation of phosphoranyl radicals by reaction of alkoxyl radicals with trivalent organophosphorus compounds as well as their follow-up fragmentation reactions have been discussed in detail in a number of reviews,[2,8−10] and useful synthetic applications based on these processes have been described.[11−13] Despite this interest, limited direct kinetic information is presently available on the reactions described in Scheme 1, with the available data being essentially limited to the reactions of the *tert*-butoxyl radical,[3b,c,4a,14−16] emphasizing in most cases the decay kinetics of the intermediate phosphoranyl radicals.[2,3b,c,4a,14,16] In particular, these data refer to phosphoranyl radicals characterized by significantly different structures,[2] a feature that does not allow a clear comprehension of the role of structural effects on these processes. Along this line, it seemed very interesting to obtain additional information on these processes, in particular, for what concerns the role of structural effects on both the attacking radical and the phosphorus compound, and for this purpose we have carried out a time-resolved kinetic study on the reactions of the cumyloxyl (CumO$^{\bullet}$) and benzyloxyl (BnO$^{\bullet}$) radicals with a series of structurally related trialkyl phosphites ($(RO)_3P$: R = Me, Et, *i*-Pr, *t*-Bu) and on the β-fragmentation reactions of the intermediate tetraalkoxyphosphoranyl radicals thus formed.

Another point of interest is represented by the fact that triaryl phosphites have found value as antioxidant additives to polymers[17] and provide in particular a convenient method for the generation of phenoxyl radicals via homolytic substitution promoted by alkoxyl radicals (Scheme 1, path a, L = OAr).[2,3a,5b,18,19] To our knowledge, however, no absolute measurement of the rate constants for reaction of alkoxyl radicals with triaryl phosphites is presently available. Accordingly, we have considered it of interest to study also the reactions of CumO$^{\bullet}$ with triphenyl and tris(2,4-di-*tert*-butylphenyl) phosphite ($(ArO)_3P$: Ar = C_6H_5, 2,4-$(t\text{-Bu})_2C_6H_3$).[20]

Results and Discussion

t-BuO$^{\bullet}$, CumO$^{\bullet}$, and BnO$^{\bullet}$ have been generated by 266 nm laser flash photolysis (LFP) of argon- or nitrogen-saturated MeCN solutions at T = 25 °C containing di-*tert*-butyl, dicumyl, and dibenzyl peroxide, respectively (eq 1).

$$\mathrm{RO{-}OR} \xrightarrow[266\ \mathrm{nm}]{h\nu} 2\ \mathrm{RO}^{\bullet} \qquad (1)$$

$$\mathrm{R} = \begin{array}{l} \mathrm{C(CH_3)_3} \\ \mathrm{PhC(CH_3)_2} \\ \mathrm{PhCH_2} \end{array}$$

In some experiments, CumO$^{\bullet}$ has also been generated by 355 nm LFP of nitrogen-saturated MeCN, benzene, chlorobenzene, or CCl_4 solutions at T = 25 °C containing dicumyl peroxide.

As described previously, in MeCN solution *t*-BuO$^{\bullet}$ is characterized by a relatively weak UV band centered at 280 nm,[21,22] while CumO$^{\bullet}$ and BnO$^{\bullet}$ are characterized by a broad absorption band in the visible region of the spectrum centered at 485 and 460 nm, respectively.[22,23] Under these conditions, *t*-BuO$^{\bullet}$ and CumO$^{\bullet}$ decay mainly by C−CH_3 β-scission,[21,22,24] while the decay of BnO$^{\bullet}$ can be mainly attributed to hydrogen atom abstraction from the solvent.[25,26]

Reactions with Trialkyl Phosphites $(RO)_3P$. The reactions of CumO$^{\bullet}$ and BnO$^{\bullet}$ with trialkyl phosphites have been studied by LFP. Figure 1 shows the time-resolved absorption spectra observed after 266 nm LFP of an argon-saturated MeCN solution (T = 25 °C) containing dicumyl peroxide 10 mM and triisopropyl phosphite ($(i\text{-PrO})_3P$) 1.15 mM.

The time-resolved spectrum recorded 64 ns after the laser pulse (filled circles) shows the characteristic cumyloxyl radical absorption band centered at 485 nm.[22,23] The decay of this band (inset b), which is accelerated by the presence of $(i\text{-PrO})_3P$, is accompanied by the formation of a species (384 ns, empty circles) characterized by an absorption band that extends from 340 nm toward the UV region, that, by comparison with literature data,[15] is assigned to the tetraalkoxyphosphoranyl radical, CumOP$^{\bullet}$(O*i*-Pr)$_3$, formed following addition of CumO$^{\bullet}$ to the phosphorus center as described in Scheme 2, path a. This radical in turn decays (inset a) leading to a stable species assigned to triisopropyl phosphate O=P(O-*i*-Pr)$_3$, formed after Cum−O β-scission in the intermediate tetraalkoxyphosphoranyl radical (Scheme 2, path b).[27]

An analogous behavior has been also observed in the reactions of CumO$^{\bullet}$ and BnO$^{\bullet}$ with the other trialkyl phosphites, where in all cases the decay of the alkoxyl radical visible absorption band is accompanied by the buildup of the pertinent tetraalkoxylphosphoranyl radical band in the UV

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(26) BnO$^{\bullet}$ undergoes a rapid 1,2-H-atom shift reaction in water and alcohols (see ref 25). Accordingly, in MeCN the decay of this radical can be accelerated by the presence of small amounts of water.

(27) A contribution to the residual absorbance also derives from the cumyl radical, which accordingly is known to display an absorption at $\lambda \leq$ 340 nm (see ref 28).

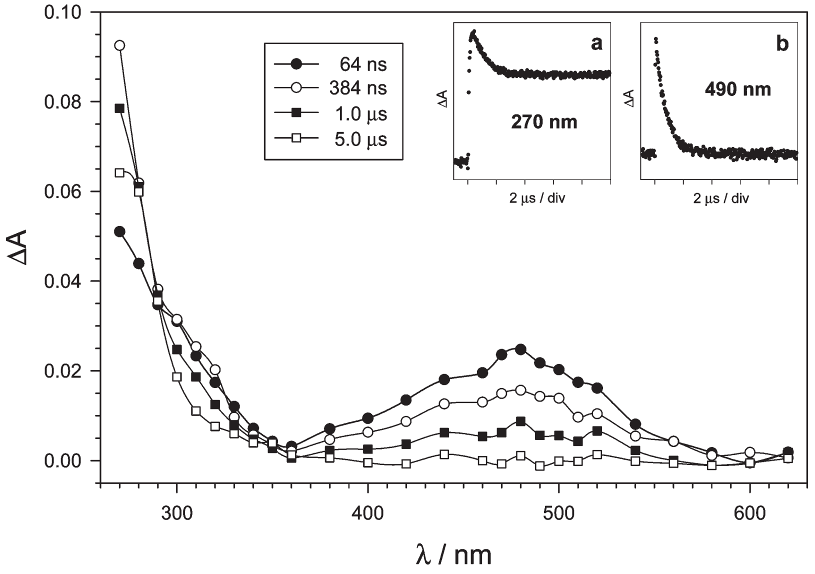
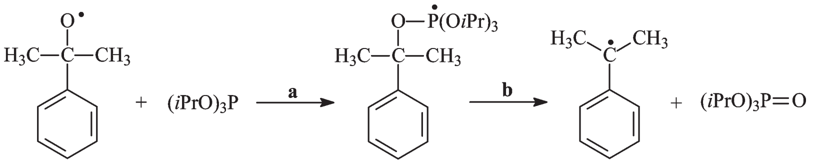


FIGURE 1. Time-resolved absorption spectra observed after 266 nm LFP of an argon-saturated MeCN solution (T = 25 °C), containing dicumyl peroxide 10 mM and triisopropyl phosphite 1.15 mM, recorded 64 ns (filled circles), 384 ns (empty circles), 1.0 μs (filled squares), and 5.0 μs (empty squares) after the laser pulse (8 ns, 10 mJ). Insets: (a) buildup and consequent decay of absorbance monitored at 270 nm; (b) decay of absorbance monitored at 490 nm.

SCHEME 2



region, followed by its decay. The time-resolved spectra observed after reaction of CumO$^•$ with $(MeO)_3P$ and $(EtO)_3P$, and of BnO$^•$ with $(EtO)_3P$, are reported in the Supporting Information, Figures S1−S3.

Kinetic studies have been carried out by LFP following the decay of the CumO$^•$ and BnO$^•$ visible absorption bands at 490 and 460 nm, respectively. When the observed rate constants (k_{obs}) have been plotted against the trialkyl phosphite concentration, excellent linear dependencies have been observed, and the second-order rate constants for addition of the alkoxyl radicals to the trialkyl phosphites (k_A) have been obtained from the slopes of these plots. The plots of k_{obs} vs [(i-PrO)$_3$P] for the reactions of CumO$^•$ (filled circles) and BnO$^•$ (empty circles) are shown in Figure 2. Additional plots for the reactions of both CumO$^•$ and BnO$^•$ with the trialkyl phosphites are reported in the Supporting Information (Figures S6−S15).

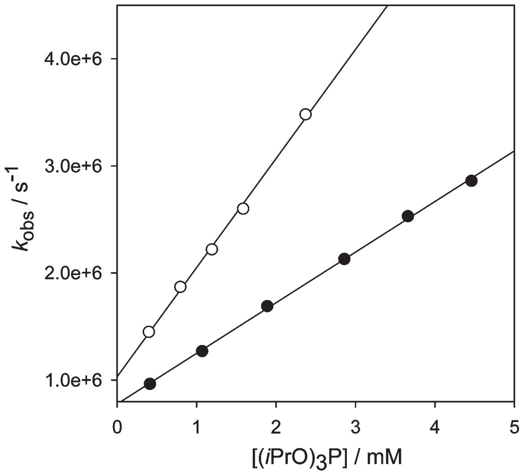


FIGURE 2. Plots of k_{obs} vs [(i-PrO)$_3$P] for the reactions of the cumyloxyl radical (filled circles) and of the benzyloxyl radical (empty circles), carried out in argon-saturated acetonitrile solution at T = 25 °C. From the linear regression: CumO$^•$ + (i-PrO)$_3$P intercept 7.8×10^5 s^{-1}, slope 4.73×10^8 M^{-1} s^{-1}, r^2 = 0.9993. BnO$^•$ + (i-PrO)$_3$P intercept 1.0×10^6 s^{-1}, slope 1.02×10^9 M^{-1} s^{-1}, r^2 = 0.9979.

All of the kinetic data thus obtained are collected in Table 1. Also included in Table 1 are some kinetic data measured in different solvents for the reactions of CumO$^•$ with $(MeO)_3P$, determined, due to solvent absorption at 266 nm, employing 355 nm LFP for the generation of CumO$^•$.

The data displayed in Table 1 show that the reaction between CumO$^•$ and the trialkyl phosphites $(RO)_3P$ is influenced by the nature of the alkyl group R, slightly decreasing on going from R = Me ($k_A = 6.2 \times 10^8$ M^{-1} s^{-1}) to R = i-Pr ($k_A = 4.7 \times 10^8$ M^{-1} s^{-1}), with the decrease in reactivity reaching 1 order of magnitude when R = t-Bu ($k_A = 5.5 \times 10^7$ M^{-1} s^{-1}). This behavior reasonably reflects the increased steric hindrance around the phosphorus center that disfavors the addition of the alkoxyl radical.

The second-order rate constant measured for reaction of CumO$^•$ with $(EtO)_3P$ ($k_A = 5.6 \times 10^8$ M^{-1} s^{-1}) can be

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TABLE 1. Second-Order Rate Constants (k_A) for the Reactions of the Cumyloxyl (CumO$^•$) and Benzyloxyl Radical (BnO$^•$) with Trialkyl Phosphites, Measured at T = 25 °C[a]

reaction	solvent	λ_{ex}[b] (nm)	k_A/M^{-1} s^{-1} [c]
CumO$^•$ + (MeO)$_3$P	MeCN	266	$6.2 \pm 0.1 \times 10^8$
		355	$5.7 \pm 0.1 \times 10^8$
	benzene	355	$5.8 \pm 0.2 \times 10^8$
	PhCl	355	$5.75 \pm 0.05 \times 10^8$
	CCl$_4$	355	$5.5 \pm 0.1 \times 10^8$
BnO$^•$ + (MeO)$_3$P	MeCN	266	$1.1 \pm 0.1 \times 10^9$
CumO$^•$ + (EtO)$_3$P	MeCN	266	$5.6 \pm 0.1 \times 10^8$
BnO$^•$ + (EtO)$_3$P	MeCN	266	$1.1 \pm 0.1 \times 10^9$
CumO$^•$ + (*i*-PrO)$_3$P	MeCN	266	$4.7 \pm 0.1 \times 10^8$
BnO$^•$ + (*i*-PrO)$_3$P	MeCN	266	$1.0 \pm 0.1 \times 10^9$
CumO$^•$ + (*t*-BuO)$_3$P	MeCN	266	$5.5 \pm 0.5 \times 10^7$
BnO$^•$ + (*t*-BuO)$_3$P	MeCN	266	$3.9 \pm 0.2 \times 10^8$

[a] LFP 266 nm, Ar- or N$_2$-saturated, [dicumyl peroxide] = 10 mM or [dibenzyl peroxide] = 8 mM, [(RO)$_3$P] = 0.2−23 mM. LFP 355 nm, Ar or N$_2$-saturated, [dicumyl peroxide] = 1 M. [b] Excitation wavelength. [c] Determined from the slope of the k_{obs} vs [(RO)$_3$P] plots, where in turn k_{obs} values have been measured following the decay of the alkoxyl radical visible absorption band at 460 nm for BnO$^•$ and 490 nm for CumO$^•$. Average of at least two determinations.

TABLE 2. First-Order Rate Constants for Fragmentation of Tetralkoxyphosphoranyl Radicals, Measured at T = 25 °C[a]

radical	k_β[b]/s^{-1}
CumOP$^•$(OMe)$_3$	4.6×10^6
BnOP$^•$(OMe)$_3$	4.0×10^6
t-BuOP$^•$(OMe)$_3$	5.6×10^5
CumOP$^•$(OEt)$_3$	6.3×10^6
BnOP$^•$(OEt)$_3$	4.5×10^6
t-BuOP$^•$(OEt)$_3$	7.9×10^5
CumOP$^•$(O*i*-Pr)$_3$	7.1×10^6
BnOP$^•$(O*i*-Pr)$_3$	5.0×10^6
t-BuOP$^•$(O*i*-Pr)$_3$	9.1×10^5

[a] Generated by 266 nm LFP of argon-saturated MeCN solutions, containing dicumyl peroxide 50 mM, dibenzyl peroxide 12 mM, or di-*tert*-butyl peroxide 0.5 M and the pertinent trialkyl phosphite ([(RO)$_3$P] between 10 and 85 mM). [b] Measured following the decay of the phosphoranyl radical at 320 nm. Error ≤10%.

compared with the previously measured values for reaction of *t*-BuO$^•$ with (EtO)$_3$P: $k_A = 8.1 \times 10^8$ M^{-1} s^{-1} (determined by ESR by competition with hydrogen atom abstraction from cyclopentane at T = 30 °C),[3c,16] and $k_A = 1.7 \times 10^9$ M^{-1} s^{-1} (determined by LFP in di-*tert*-butyl peroxide/2,2,4-trimethylpentane (7:3 v/v) at T = 28 °C, following the buildup of *t*-BuOP$^•$(OEt)$_3$ at 328 nm).[15] The values appear to be in reasonable agreement, in line with the similar reactivity generally displayed by CumO$^•$ and *t*-BuO$^•$ in a variety of reactions,[29] even though the different conditions employed do not allow a fully consistent comparison between these data.

The reaction of CumO$^•$ with (MeO)$_3$P has been also studied in different solvents and the kinetic data thus obtained clearly show the absence of any relevant kinetic solvent effect. The slight (and reproducible) decrease in reactivity observed on going from 266 to 355 nm LFP can be explained in terms of the increase in viscosity of the MeCN solution determined by the 100-fold increase in dicumyl peroxide concentration (from 0.01 to 1 M).

The second-order rate constants for reaction of BnO$^•$ with the trialkyl phosphites (RO)$_3$P are not influenced by the nature of the alkyl group when R = Me, Et, and *i*-Pr (k_A = 1.0−1.1 × 10^9 M^{-1} s^{-1}), showing instead a 2.5-fold decrease in reactivity when R = *t*-Bu ($k_A = 3.9 \times 10^8$ M^{-1} s^{-1}). These rate constants are always higher (between 2 and 7 times) than those measured for the corresponding reactions of CumO$^•$, reasonably reflecting the smaller steric demand of BnO$^•$ as compared to CumO$^•$.[30] Quite importantly, these observations clearly indicate that steric effects in both the attacking radical and the trialkyl phosphite play an important role in these processes, providing in particular a basis for the quantitative evaluation of these effects.

The trend observed in the reactions of both CumO$^•$ and BnO$^•$ appears also to be in line with the generally accepted hypothesis that the alkoxyl radical attacks the trivalent phosphorus compound from the apical position.[31]

As shown in Figure 1, the formation of the tetraalkoxyphosphoranyl radical competes with its unimolecular decay. Accordingly, by using sufficiently high trialkyl phosphite concentrations, so as to increase the rate of formation of the intermediate phosphoranyl radical, it has been possible to measure the first-order rate constants for β-scission of the R′−O (R′ = Cum, Bn) bond in the phosphoranyl radicals R′OP$^•$(OR)$_3$. These values are collected in Table 2. Also included in this Table are the kinetic data for the phosphoranyl radicals where R′ = *t*-Bu, obtained following the reaction of *t*-BuO$^•$ with the trialkyl phosphites.

The data collected in Table 2 show that for the tetraalkoxphosphoranyl radicals R′OP$^•$(OR)$_3$ the fragmentation rate constants increase (for a given alkyl group R) in the order R′ = *tert*-butyl < R′ = benzyl < R′ = cumyl, a behavior that reasonably reflects the relative stabilities of the radicals formed after β-scission.[32] Quite importantly, the observation of the tetraalkoxyphosphoranyl radicals in the reactions of both CumO$^•$ and BnO$^•$ with trialkyl phosphites is in contrast with previous reports where no intermediate phosphoranyl radical, but only the benzyl radical could be detected by ESR following reaction between BnO$^•$ and (EtO)$_3$P, even at −140 °C, a result that was interpreted in terms of an extremely fast β-scission reaction in BnOP$^•$(OEt)$_3$.[4a,33] Clearly, the observation of a ≤ 8-fold increase in k_β on going from R′ = *tert*-butyl to R′ = benzyl (and cumyl) is in contrast with this indication.

The slight increase in reactivity observed (for a given R′ group) on going from R = Me to R = *i*-Pr can be instead explained in terms of a steric relief associated to the fragmentation reaction, a hypothesis that is supported by the observation of a larger kinetic effect along the trialkyl phosphite series for R′ = *tert*-butyl and cumyl as compared to R′ = benzyl.[34] However, these steric effects appear to be of minor importance in line with previous studies by Ingold and co-workers on the β-scission of trialkoxyl(*tert*-butoxy)phosphoranyl radicals.[4a]

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[29] See, for example: Pischel, U.; Nau, W. N. *J. Am. Chem. Soc.* **2001**, *123*, 9727–9737. Valgimigli, L.; Banks, J. T.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1995**, *117*, 9966–9971. Baignée, A.; Howard, J. A.; Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 6120–6123.

[30] BnO$^•$ is expected to be more electrophilic than CumO$^•$, and accordingly, polar effects may also play a role in the addition of an alkoxyl radical to the phosphorus center.

[31] For a critical discussion on the stereochemistry of formation of phosphoranyl radicals, see, for example, ref 2.

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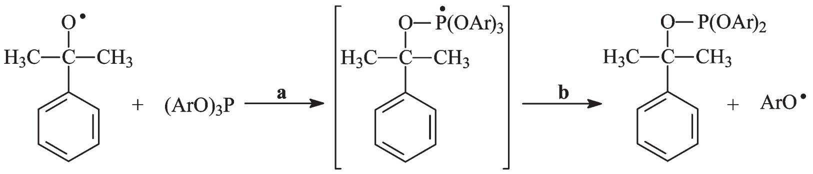
[33] Bentrude, W. G.; Min, T. B. *J. Am. Chem. Soc.* **1972**, *94*, 1025–1026.

[34] The data collected in Table 2 do not allow to draw any conclusion on the question of apical vs equatorial β-scission in the intermediate phosphoranyl radical. For a critical discussion, see refs 2, 9, and 10.

SCHEME 3



The rate constant measured for fragmentation of t-BuOP$^•$(OEt)$_3$ ($k_\beta = 7.9 \times 10^5$ s^{-1}) is in reasonable agreement with those measured previously for the same reaction:[35] $k_\beta = 3.9 \times 10^5$ s^{-1} (determined by LFP in di-*tert*-butyl peroxide/2,2,4-trimethylpentane (7:3 v/v) at T = 27 °C)[15] and $k_\beta = 2.8 \times 10^5$ s^{-1} (determined by LFPESR in di-*tert*-butyl peroxide/2,2,4-trimethylpentane (7:3 v/v) at T = 20 °C).[14]

Reactions with Triaryl Phosphites (ArO)$_3$P. The reactions of CumO$^•$ with two triaryl phosphites, namely triphenyl phosphite and tris(2,4-di-*tert*-butylphenyl) phosphite, have also been studied. With these substrates, 355 nm LFP has been employed. Figure 3 shows the time-resolved absorption spectra observed after 355 nm LFP of an argon-saturated benzene solution (T = 25 °C) containing dicumyl peroxide 1.0 M and tris(2,4-di-*tert*-butylphenyl) phosphite 10 mM.

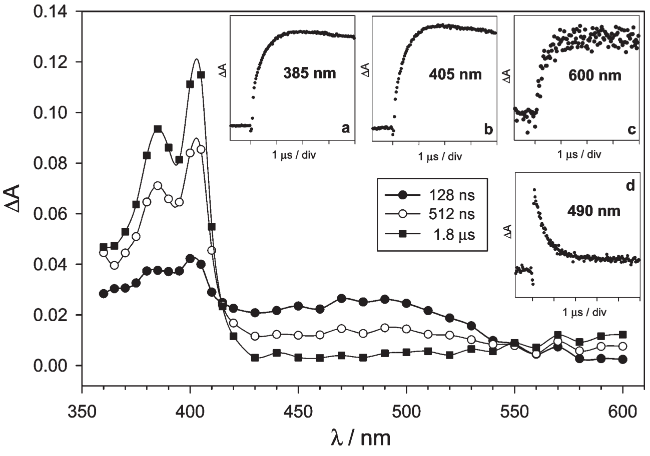


FIGURE 3. Time-resolved absorption spectra observed after 355 nm LFP of an argon-saturated benzene solution (T = 25 °C), containing dicumyl peroxide 1.0 M and tris(2,4-di-*tert*-butylphenyl) phosphite 10 mM, recorded 128 ns (filled circles), 512 ns (empty circles), and 1.8 μs (filled squares) after the laser pulse (8 ns, 10 mJ). Insets: (a) buildup of absorbance monitored at 385 nm; (b) buildup of absorbance monitored at 405 nm; (c) buildup of absorbance monitored at 600 nm; (d) decay of absorbance monitored at 490 nm.

The time-resolved spectrum recorded 128 ns after the laser pulse (filled circles) shows the characteristic cumyloxyl radical absorption band centered at 485 nm.[22,23] The decay of this band (inset d), which is accelerated by the presence of the triaryl phosphite, is accompanied by the formation of a species (1.8 μs, filled squares) characterized by two intense absorption bands at 385 and 405 nm (insets a and b) and a weak absorption band that extends from 570 nm toward the red (inset c). Two isosbestic points can be identified at 415 and 550 nm. These bands are assigned to the 2,4-di-*tert*-butylphenoxyl radical by comparison with literature data[36] and with the spectrum of this radical generated independently by hydrogen atom abstraction from 2,4-di-*tert*-butylphenol by CumO$^•$ (Figure 4).

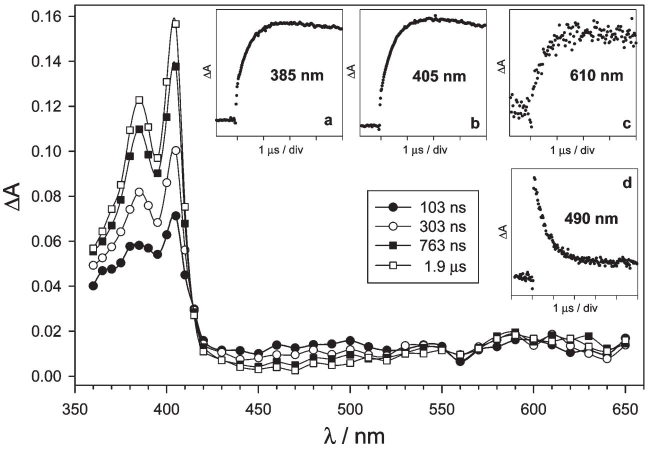


FIGURE 4. Time-resolved absorption spectra observed after 355 nm LFP of an argon-saturated benzene solution (T = 25 °C), containing dicumyl peroxide 1.0 M and 2,4-di-*tert*-butylphenol 1.2 mM, recorded 103 ns (filled circles), 303 ns (empty circles), 763 ns (filled squares), and 1.9 μs (empty squares) after the laser pulse (8 ns, 10 mJ). Insets: (a) buildup of absorbance monitored at 385 nm; (b) buildup of absorbance monitored at 405 nm; (c) buildup of absorbance monitored at 610 nm; (d) decay of absorbance monitored at 490 nm.

The formation of the 2,4-di-*tert*-butylphenoxyl radical in the reaction between CumO$^•$ and tris(2,4-di-*tert*-butylphenyl) phosphite can be explained in terms of the addition of CumO$^•$ to the phosphorus center as described in Scheme 3, path a (Ar = 2,4-di-*tert*-butylphenyl) followed by (or concerted with, see below) α-cleavage of the ArO−P bond in the intermediate phosphoranyl radical (path b).

Even though no intermediate phosphoranyl radical CumOP$^•$(OAr)$_3$ has been detected in this experiment, it is not possible to rule out the possible intermediacy of this species because its lifetime could be too short to allow detection under the experimental conditions employed: in other words, the decay of CumOP$^•$(OAr)$_3$ (if actually formed) is fast compared with its rate of formation by reaction of CumO$^•$ with tris(2,4-di-*tert*-butylphenyl) phosphite.[37]

An analogous behavior has been also observed in the reaction of CumO$^•$ with triphenyl phosphite. The time-resolved spectra observed after reaction of CumO$^•$ with

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(35) The observed differences in rate constant reasonably reflect the significantly different experimental conditions employed in these studies.

(36) Maki, T.; Araki, Y.; Ishida, Y.; Onomura, O.; Matsumura, Y. *J. Am. Chem. Soc.* **2001**, *123*, 3371–3372.

(37) It is important to point out that even though it is generally assumed that the displacement of phenoxyl radicals from triaryl phosphites by alkoxyl radicals is a concerted process, ESR evidence in favor of the formation of an intermediate phosphoranyl radical has been provided in the reactions of alkoxyl radicals with triphenyl phosphite (see ref 3a).

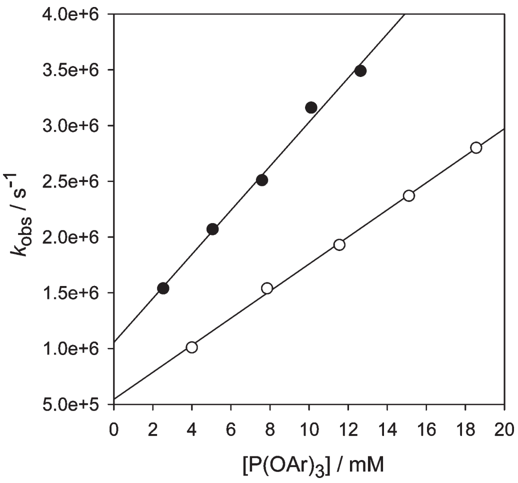

FIGURE 5. Plots of k_{obs} vs [(ArO)$_3$P] for the reactions of the cumyloxyl radical with triphenyl phosphite (filled circles) and tris(2,4-di-*tert*-butylphenyl) phosphite (empty circles), carried out in argon-saturated benzene solution at T = 25 °C. From the linear regression analysis: CumO$^{\bullet}$ + (PhO)$_3$P intercept 1.0×10^6 s^{-1}, slope 1.98×10^8 M^{-1} s^{-1}, r^2 = 0.9930. CumO$^{\bullet}$ + (ArO)$_3$P (Ar = 2,4-di-*tert*-butylphenyl) intercept 5.5×10^5 s^{-1}, slope 1.21×10^8 M^{-1} s^{-1}, r^2 = 0.9987.

(PhO)$_3$P and PhOH are reported in the Supporting Information, Figures S4 and S5, respectively.

Kinetic studies have been carried out by LFP following the decay of the CumO$^{\bullet}$ visible absorption band at 490 nm. When the observed rate constants (k_{obs}) have been plotted against the triaryl phosphite concentration, excellent linear dependencies have been observed, and the second-order rate constants for reaction of CumO$^{\bullet}$ with trialkyl phosphites (k_A) have been obtained from the slopes of these plots. The plots of k_{obs} vs [(ArO)$_3$P] for the reactions of CumO$^{\bullet}$ with triphenyl phosphite (filled circles) and tris(2,4-di-*tert*-butylphenyl) phosphite (empty circles) in benzene solution are shown in Figure 5. Additional plots for the reactions of CumO$^{\bullet}$ with triphenyl phosphite in different solvents and for the reactions of CumO$^{\bullet}$ with phenol and 2,4-di-*tert*-butylphenol are reported in the Supporting Information (Figures S16−S22).

All of the kinetic data thus obtained are collected in Table 3. As a matter of comparison, Table 3 also contains the second-order rate constants for reaction of CumO$^{\bullet}$ with phenol and 2,4-di-*tert*-butylphenol.

The data displayed in Table 3 show that the reaction between CumO$^{\bullet}$ and the triaryl phosphites (ArO)$_3$P is influenced to a limited extent by the nature of the aryl group, with the rate constant measured in benzene solution that almost halves on going from Ar = Ph (k = 2.05×10^8 M^{-1} s^{-1}) to Ar = 2,4-di-*tert*-butylphenyl (k = 1.18×10^8 M^{-1} s^{-1}). This result indicates that the presence of the bulky *tert*-butyl substituents on the aromatic rings does not increase significantly the steric hindrance around the phosphorus center that undergoes addition by CumO$^{\bullet}$, again in line with the hypothesis outlined above of an alkoxyl radical attack to the triaryl phosphite from the apical position.

TABLE 3. Second-Order Rate Constants (k_A) for Reaction of the Cumyloxyl Radical (CumO$^{\bullet}$) with Triaryl Phosphites and Phenols, Measured at T = 25 °C in Different Solvents[a]

reaction	solvent	k^b/M^{-1} s^{-1}
CumO$^{\bullet}$ + (PhO)$_3$P	MeCN	$2.5 \pm 0.1 \times 10^8$
	benzene	$2.05 \pm 0.05 \times 10^8$
	PhCl	$2.41 \pm 0.02 \times 10^8$
	CCl$_4$	$2.78 \pm 0.02 \times 10^8$
CumO$^{\bullet}$ + (ArO)$_3$P [c]	benzene	$1.18 \pm 0.04 \times 10^8$
CumO$^{\bullet}$ + PhOH	MeCN	$1.10 \pm 0.02 \times 10^7$
	benzene	$3.15 \pm 0.05 \times 10^8$
	CCl$_4$	$5.7 \pm 0.2 \times 10^8$
CumO$^{\bullet}$ + ArOH [c]	benzene	$1.00 \pm 0.02 \times 10^9$

[a]LFP 355 nm, argon-saturated, [dicumyl peroxide] = 1.0 M. [b]Determined from the slope of the k_{obs} vs [(ArO)$_3$P] or [ArOH] plots, where in turn the k_{obs} values have been measured following the decay of the CumO$^{\bullet}$ visible absorption band at 490 nm. Average of at least two determinations. [c]Ar = 2,4-di-*tert*-butylphenyl.

Very importantly, these data represent the first determination of the absolute rate constants for reaction of triaryl phosphites with alkoxyl radicals, clearly indicating that such substrates efficiently quench alkoxyl radicals, with the measured rate constants that are relatively close to those observed for the reactions of alkoxyl radicals with a variety of phenols.[38] These data provide, moreover, a quantitative evaluation of the efficiency of triaryl phosphites as radical scavenging antioxidants.[39]

The reaction of CumO$^{\bullet}$ with (PhO)$_3$P has been also studied in different solvents, and the kinetic data thus obtained clearly show the absence of relevant kinetic solvent effects. This result is in contrast with the well-known solvent effect on the hydrogen abstraction reactions of alkoxyl radicals from phenols,[38,40] where hydrogen-bonding interactions between the phenolic hydrogen atom and the solvent have been shown to play a key role.[41] A similar effect is clearly not possible with substrates that cannot act as hydrogen bond donors such as triaryl phosphites.

The comparison between the rate constants obtained for the two triaryl phosphites and for the corresponding phenols in benzene evidence opposite behaviors, with the k values measured for the latter substrates that show an approximately 3-fold increase on going from phenol (k = 3.15×10^8 M^{-1} s^{-1}) to 2,4-di-*tert*-butylphenol (k = 1.00×10^9 M^{-1} s^{-1}). In a non-hydrogen-bonding donor solvent such as benzene, this behavior can be explained in terms of the difference in O−H BDE between the two phenols that decreases on going from phenol (BDE = 86.7 kcal mol^{-1})[42] to 2,4-di-*tert*-butylphenol (BDE = 84.7 kcal mol^{-1}).[43,44]

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[38] See, for example: Snelgrove, D. W.; Lusztyk, J.; Banks, J. T.; Peter Mulder, P.; Ingold, K. U. *J. Am. Chem. Soc.* **2001**, *123*, 469–477. and references cited therein.

[39] It is important to mention that as compared to phenolic antioxidants, triaryl phosphites are able, at least in principle, to scavenge 3 equiv of alkoxyl radicals.

[40] Litwinienko, G.; Ingold, K. U. *Acc. Chem. Res.* **2007**, *40*, 222–230.

[41] The second-order rate constants for hydrogen atom abstraction by CumO$^{\bullet}$ from phenol displayed in Table 3 are somewhat different from those given in ref 38, determined for the same reaction in the same solvents (k_H = 86, 28, and 0.58×10^7 M^{-1} s^{-1}, in CCl$_4$, benzene, and MeCN, respectively). We can reasonably attribute these differences to variations in solvent polarity (and in the solvent hydrogen-bond acceptor ability) induced by the high concentration of dicumyl peroxide (1.0 M) employed in these experiments. Accordingly, we have observed that the empirical solvent polarity parameter $E_T{}^{30}$ (for a definition, see: Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; Wiley-VCH: Weinheim, 2003) decreases by 1.4 units on going from MeCN to a 1.0 M solution of dicumyl peroxide in MeCN, and an opposite effect (i.e., an increase in polarity) can be reasonably expected in the case of CCl$_4$.

[42] Mulder, P.; Korth, H.-G.; Pratt, D. A.; DiLabio, G. A.; Valgimigli, L.; Pedulli, G. F.; Ingold, K. U. *J. Phys. Chem. A* **2005**, *109*, 2647–2655.

In conclusion, the kinetic data obtained for the reactions of alkoxyl radicals with a series of trialkyl phosphites clearly show that the addition reaction leads to the formation of intermediate tetraalkoxyphosphoranyl radicals and, in particular, that steric effects in both the attacking radical and the trialkyl phosphite play an important role. Steric effects are instead of minor importance in the β-scission of the phosphoranyl radicals, where the reaction appears to be governed by the relative stabilities of the radicals formed after fragmentation. Absolute rate constants for reaction of the cumyloxyl radical with triaryl phosphites have been measured for the first time, and the values obtained indicate that these substrates are able to quench alkoxyl radicals with efficiencies that are comparable to those displayed by many phenols.

Experimental Section

Materials. Acetonitrile, benzene, chlorobenzene, and carbon tetrachloride used in the kinetic experiments were spectroscopic grade solvents.

Trimethyl phosphite, triethyl phosphite, triphenyl phosphite, tris(2,4-di-*tert*-butylphenyl) phosphite, phenol, and 2,4-di-*tert*-butylphenol were of the highest commercial quality available and were used as received. Triisopropyl phosphite was purified by distillation prior to use.

Tri-*tert*-butyl phosphite was prepared by reaction of PCl_3 with 2-methyl-2-propanol in anhydrous THF, in the presence of triethylamine, according to a previously described procedure.[45] Care was taken to avoid heating and air exposure of the product that was always handled under inert atmosphere and stored under nitrogen at $T = -20$ °C. The purity of the sample was checked by ^{1}H NMR prior to every kinetic experiment. ^{1}H NMR ($CDCl_3$): δ 1.38 (s, $(CH_3)_3C$).

Dicumyl peroxide and di-*tert*-butyl peroxide were of the highest commercial quality available and were used as received.

Dibenzyl peroxide was prepared in small portions by reaction of KO_2 with benzyl bromide in dry benzene, in the presence of 18-crown-6 ether, according to a previously described procedure.[25,46] The product was purified by column chromatography (silica gel, eluent hexane/dichloromethane 1:1) and identified by ^{1}H NMR. ^{1}H NMR ($CDCl_3$):[25] δ 7.34 (s, 10H, ArH), 4.95 (s, 4H, CH_2).

Laser Flash Photolysis Studies. Laser flash photolysis (LFP) experiments were carried out with a laser kinetic spectrometer using the third harmonic (355 nm) or the fourth harmonic (266 nm) of a Q-switched Nd:YAG laser, delivering 8 ns pulses. The laser energy was adjusted to ≤ 10 mJ/pulse by the use of the appropriate filter. A 3 mL Suprasil quartz cell (10 mm $\times$ 10 mm) was used for all experiments. Argon- or nitrogen-saturated solutions of the peroxides (0.008−1.0 M) were used. In the 266 nm LFP experiments, concentrations of dicumyl peroxide and dibenzyl peroxide of 10 and 8 mM, respectively, were employed. In the 355 nm LFP experiments, carried out for the reactions of $\mathrm{CumO}^{\bullet}$ with $(MeO)_3P$ in acetonitrile, benzene, chlorobenzene, and carbon tetrachloride, and in the reactions of $\mathrm{CumO}^{\bullet}$ with triphenyl phosphite, tris(2,4-di-*tert*-butylphenyl) phosphite, phenol, and 2,4-di-*tert*-butylphenol in acetonitrile and/or benzene, a 1 M concentration of dicumyl peroxide was instead employed.

All of the experiments were carried out at $T = 25 \pm 0.5$ °C under magnetic stirring. First-order or pseudo-first-order rate constants were obtained by averaging four to eight individual values and were reproducible to within 5%.

Second-order rate constants for the reactions of the cumyloxyl ($\mathrm{CumO}^{\bullet}$) or benzyloxyl ($\mathrm{BnO}^{\bullet}$) radicals with the trialkyl and triaryl phosphites ($(RO)_3P$: R = Me, Et, *i*-Pr, *t*-Bu; $(ArO)_3P$: Ar = C_6H_5, 2,4-(t-Bu)$_2C_6H_3$) were obtained from the slopes of the k_{obs} (measured following the decay of the $\mathrm{CumO}^{\bullet}$ or $\mathrm{BnO}^{\bullet}$ visible absorption band at 490 and 460 nm, respectively) vs $[(RO)_3P]$ or $[(ArO)_3P]$ plots. Fresh solutions were used for every $(RO)_3P$ or $(ArO)_3P$ concentration. Correlation coefficients were in all cases > 0.992. The given rate constants are the average of at least two independent experiments, typical errors being $< 10\%$.

The first-order rate constants for fragmentation of the tetraalkoxyphosphoranyl radicals were measured following the decay of the phosphoranyl radical at 320 nm. Sufficiently high concentrations of $(RO)_3P$ were used, in order to make the formation of the phosphoranyl radical significantly faster than its decay. In the reactions with $\mathrm{CumO}^{\bullet}$ concentrations of $(RO)_3P$ ranging between 50 and 85 mM were employed. In the reactions with $\mathrm{BnO}^{\bullet}$ concentrations of $(RO)_3P$ ranging between 10 and 35 mM were employed. In the reactions with $t\text{-BuO}^{\bullet}$ concentrations of $(RO)_3P$ ranging between 10 and 45 mM were employed. In order to ensure significant absorption of the 266 nm laser light by the precursor peroxides at these relatively high $[(RO)_3P]$, the following concentrations were used in these experiments: dicumyl peroxide 50 mM, dibenzyl peroxide 12 mM, di-*tert*-butyl peroxide 0.5 M.

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Supporting Information Available: Time-resolved absorption spectra observed after reaction of the cumyloxyl radical with $(MeO)_3P$, $(EtO)_3P$, $(PhO)_3P$, and PhOH and after reaction of the benzyloxyl radical with $(EtO)_3P$. Plots of k_{obs} vs $[(RO)_3P]$, k_{obs} vs $[(ArO)_3P]$, and k_{obs} vs [ArOH] for the reactions of the cumyloxyl and benzyloxyl radicals. This material is available free of charge via the Internet at http://pubs.acs.org.

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(43) Ribeiro da Silva, M. A. V.; Matos, M. A. R.; Morais, V. M. F.; Miranda, M. S. *J. Org. Chem.* **1999**, *64*, 8816–8820.

(44) Additivity values predict a difference in O−H BDE between these two phenols of 3.1 kcal mol^{-1}. See: Wright, J. S.; Johnson, E. R.; DiLabio, G. A. *J. Am. Chem. Soc.* **2001**, *123*, 1173–1183.

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(46) Johnson, R. A.; Nidy, E. G. *J. Org. Chem.* **1975**, *40*, 1680–1681.