Electronic Absorption Spectra of Some Alkoxyl Radicals. An Experimental and Theoretical Study[1]

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Abstract: The visible and UV absorptions of a variety of alkoxyl radicals have been examined by experiment and theory. In most solvents, the *tert*-butoxyl radical shows only a weak "tail-end" absorption in the UV region of the spectrum and no absorption in the visible region. However, a visible absorption band has been observed (λ_{max} = 440 nm) in the presence of 1,3,5-trimethoxybenzene. This absorption band provides the first unequivocal evidence for the existence of alkoxyl radical/electron-rich aromatic π-complexes. By way of contrast, a solvent-independent absorption in the visible is observed for (arylcarbinyl)oxyl radicals, e.g., benzyloxyl (λ_{max} = 460 nm, ϵ = 1300 M^{-1} cm^{-1}) and cumyloxyl (λ_{max} = 485 nm, ϵ = 1300 M^{-1} cm^{-1}). Electron-donating substituents on the aromatic ring shift the visible absorption to the red by 25–30 nm for a 4-methyl group and by 100–105 nm for a 4-methoxy group. However, α-substitution has only a minor effect on λ_{max}, e.g., 530 and 535 nm for diphenylmethoxyl and 1,1-diphenylethoxyl, respectively. The visible absorption appears to be virtually uninfluenced by the (calculated) magnitude of the dihedral angle, θ, between the C–O$^\bullet$ bond and the plane of the aromatic ring, e.g., indan-1-oxyl, $\theta \sim 51°$, λ_{max} = 530 nm, and Tetralin-1-oxyl, $\theta \sim 33°$ (major conformer), λ_{max} = 520 nm, vs benzyloxyl and cumyloxyl, both of which have $\theta \sim 0°$. All of these experimental observations are well-matched by theory, which reveals that the visible absorptions of (arylcarbinyl)oxyl radicals are due to $D_0(A'') \rightarrow D_2(A'')$ ($\pi \rightarrow \pi^*$) transitions which increase the negative charge on the oxygen atom and have respectable oscillator strengths. The unpaired electron is largely localized in the oxygen 2p orbital which is perpendicular to the plane of the aromatic ring.

Our unexpected and exciting discovery that the arylcarbinyloxyl radicals, benzyloxyl, cumyloxyl, and (4-methoxycumyl)oxyl, have strong absorptions in the visible region of the spectrum[5] has led us to study a wider variety of organic radicals having the general formula ArXY$^\bullet$ (where X and Y are from the first row of the periodic table) using experimental and theoretical procedures. The results of these studies are reported herein.

Results

Experimental Studies on Alkoxyl Radicals. The alkoxyl radicals of interest were generated at room temperature by direct 308 and (when the solvent permitted) 266 nm laser flash photolysis (LFP) of symmetric and asymmetric peroxides, hyponitrites, and hydroperoxides:

$$\mathrm{ROOR} \xrightarrow[\text{308 and 266 nm}]{h\nu} 2\mathrm{RO}^\bullet \qquad \text{(method 1)}$$

$$\mathrm{ROOCMe_3} \xrightarrow[\text{308 and 266 nm}]{h\nu} \mathrm{RO}^\bullet + \mathrm{Me_3CO}^\bullet \qquad \text{(method 2)}$$

$$\mathrm{RON{=}NOR} \xrightarrow[\text{308 and 266 nm}]{h\nu} 2\mathrm{RO}^\bullet + \mathrm{N_2} \qquad \text{(method 3)}$$

$$\mathrm{ROOH} \xrightarrow[\text{266 nm only}]{h\nu} \mathrm{RO}^\bullet + \mathrm{HO}^\bullet \qquad \text{(method 4)}$$

Some alkoxyl radicals were also generated by the photosensitized decomposition of hyponitrites[6] (355 nm LFP, xanthone triplet, Xtn^3):

$$\mathrm{Xtn} \xrightarrow[\text{355 nm}]{h\nu} \mathrm{Xtn}^3$$

$$\mathrm{RON{=}NOR} + (\mathrm{Xtn}^3) \rightarrow 2\mathrm{RO}^\bullet + \mathrm{N_2} + \mathrm{Xtn} \quad \text{(method 5)}$$

***tert*-Butoxyl radicals** were generated by methods 1 (= 2) and 3. As is well-known,[5,7] these radicals have no absorption in the visible and show only a weak "tail-end" absorption in the near UV,[8] a fact which led to the mistaken belief that no alkoxyl radical would exhibit an absorption in the visible.[9] This "tail-end" absorption is red-shifted in aromatic solvents (C_6H_6 and C_6H_5Cl) relative to nonaromatic solvents (CCl_4 and CH_3CN), which suggested to us that *tert*-butoxyl radicals might form π-complexes with some aromatic molecules, i.e.,

$$\mathrm{Me_3CO}^\bullet + \mathrm{Ar} \rightleftarrows \mathrm{Me_3CO}^{\delta-}\cdot\mathrm{Ar}^{\delta+}$$

The concept of a *tert*-butoxyl radical/benzene π-complex was first put forward by Russell[10] on certain kinetic grounds[11] and

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[5] Avila, D. V.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 6576–6577.

[6] Mendenhall, G. D.; Stewart, L. C.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5109–5114.

[7] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C.; Woynar, H. *J. Am. Chem. Soc.* **1981**, *103*, 3231–3232.

[8] The absorption spectrum of this radical is shown in Figure 1 of ref 5.

[9] (a) Falvey, D. E.; Khambatta, B. S.; Schuster, G. B. *J. Phys. Chem.* **1990**, *94*, 1056–1059. (b) See also references cited therein.

[10] Russell, G. A. *J. Org. Chem.* **1959**, *24*, 300–302.

[11] See also: Walling, C.; Wagner, P. *J. Am. Chem. Soc.* **1964**, *86*, 3368–3375. See also ref 6 above.

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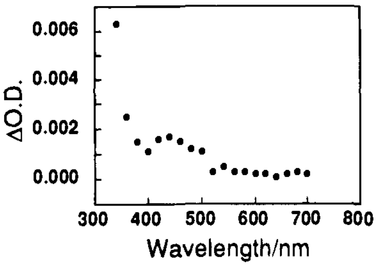

Figure 1. Transient absorption spectrum measured 0.4 μs after 308 nm LFP of 0.16 M di-*tert*-butyl peroxide in CH_3CN containing 0.6 M 1,3,5-trimethoxybenzene.

by analogy with the then already established[12,13] chlorine atom/benzene π-complex. However, in contrast to the massive spectroscopic evidence favoring the formation of $Cl^{\bullet}$/aromatic π-complexes,[13,14] there has been no spectroscopic search for a *tert*-butoxyl/benzene π-complex.

In view of the "red-shift" of *tert*-butoxyl's tail-end absorption in benzene and chlorobenzene, we decided to undertake a brief spectroscopic search for a *tert*-butoxyl/aromatic π-complex. The equilibrium between "free" *tert*-butoxyl and any *tert*-butoxyl/aromatic π-complex might be expected to shift more in favor of the complex as the electron density in the aromatic ring increases. The stronger the complex, the more likely it will be that a charge transfer band would be observable since it might shift into the visible region of the spectrum and increase in overall intensity. With these ideas in mind, we examined the effect of added 1,3,5-trimethoxybenzene on the absorption spectrum of *tert*-butoxyl radicals in CH_3CN.

To di-*tert*-butyl peroxide (0.16 M) in CH_3CN (OD = 0.30 at 308 nm in our reaction cell) was added 0.6 M 1,3,5-trimethoxybenzene (which increased the 308 nm OD to 0.40). Upon 308 nm LFP of this solution the same spectrum was obtained in the absence of oxygen (nitrogen purge) as under oxygen saturation (760 Torr). This spectrum showed the usual *tert*-butoxyl "tail-end" absorption together with another weak absorption at 440 nm see (Figure 1). The ratio of the 320 to 440 nm absorption intensities was 1:0.085. The 440 nm band did not appear when 0.6 M 1,3,5-trimethoxybenzene in deoxygenated or oxygenated CH_3CN was subjected to 308 nm LFP in the absence of di-*tert*-butyl peroxide. Furthermore, this long-wavelength band cannot be due to the 1,3,5-trimethoxybenzene radical cation,

$$(CH_3)_3CO^{\bullet} + (CH_3O)_3C_6H_3 \not\longrightarrow (CH_3)_3CO^{-} + [(CH_3O)_3C_6H_3)]^{\bullet +}$$

because this radical cation is known to absorb at 540 and 580 nm.[15] In addition, the 440 nm band cannot be due to the radical formed by H-atom abstraction from one of the methoxyl groups,

$$(CH_3)_3CO^{\bullet} + (CH_3O)_3C_6H_3 \rightarrow (CH_3)_3COH + (CH_3O)_2C_6H_3OCH_2^{\bullet}$$

because this absorption band appears "instantaneously" after the laser pulse. If the 440 nm band had been due to the $(CH_3O)_2C_6H_3OCH_2^{\bullet}$ radical, it would have "grown in" over the course of ca. 3 μs[16] rather than appearing within 8 ns. Further proof that the 440 nm absorption is not due to the $(CH_3O)_2C_6H_3OCH_2^{\bullet}$ radical was obtained by showing that the rate at which the signal decayed was not influenced by oxygen (saturation at 760 Torr). This was also true for the tail-end absorption of *tert*-butoxyl (monitored at 320 nm).

Table 1. Visible Absorption Band Maximum Wavelengths and Extinction Coefficients for Some Alkoxyl Radicals[a]

radical	λ_{max}/nm	ϵ/M^{-1} cm^{-1} [b,c]	$\Delta OD_{vis}/\Delta OD_{320}$ [c]
tert-butoxyl	<320		
cumyloxyl	485	1300	0.72
(4-methylcumyl)oxyl	510	1480	0.61
(4-methoxycumyl)oxyl	590	1550	0.74
benzyloxyl	460	1300	0.62
(4-methylbenzyl)oxyl	490	nd[d]	nd[d]
(4-methoxybenzyl)oxyl	560	nd	nd
Tetralin-1-oxyl	520	nd	0.55
indan-1-oxyl	530	nd	0.49
diphenylmethoxyl	530	nd	1.1
diphenylethoxyl	535	nd	1.2[e]

[a] λ_{max} does not depend on the solvent (see text). [b] Extinction coefficient of the visible absorption. [c] In CH_3CN with the alkoxyl radicals generated by 266 nm LFP of appropriate precursors. [d] Not determined. [e] Measured under O_2-saturation conditions to quench the growing in of the rearranged carbon-centered radical.

The foregoing appears to us to provide the first spectroscopic evidence for the existence of alkoxyl radical/aromatic π-complexes. Since we have previously demonstrated that solvents have no measurable effect on the rate of H-atom abstraction by cumyloxyl radicals from cyclohexane, the rate constant for this reaction being $(1.2 \pm 0.1) \times 10^6$ M^{-1} s^{-1} in a wide range of solvents,[17] we thought it would be worthwhile to check if this was also the case for the *tert*-butoxyl radical/0.6 M 1,3,5-trimethoxybenzene/cyclohexane/acetonitrile system. Unfortunately, the 440 nm absorption was too weak to carry out a detailed kinetic analysis, but a crude two-point plot ($[c\text{-}C_6H_{12}]$ = 0.0 and 3.24 M, $k_{exptl} = 4.8 \times 10^5$ s^{-1} and 3.3×10^6 s^{-1}, respectively) yielded a rate constant for the *apparent* reaction of the *tert*-butoxyl radical/1,3,5-trimethoxybenzene π-complex equal to 9×10^5 M^{-1} s^{-1} at 25 °C. Considering the likely experimental errors, this rate constant must be considered to be equal to a value reported for H-atom abstraction from cyclohexane by the noncomplexed *tert*-butoxyl radical, viz.,[18] 1.6×10^6 M^{-1} s^{-1} at 27 °C (see Discussion).

Cumyloxyl radicals were generated by methods 1, 3, and 5. The visible and UV absorptions of these radicals[8] grow in "instantaneously" upon direct photolysis (methods 1 and 3) on the nanosecond LFP time scale (~4 or 8 ns) in CCl_4, CH_3CN, $CH_3C(O)OH$, $(CH_3)_3COH$, $c\text{-}C_6H_{12}$, C_6H_6, and C_6H_5Cl, with no significant shift in the visible absorption maximum (485 nm, see Table 1) over this range of solvents. In a pair of carefully matched experiments involving the 308 nm LFP of dicumyl peroxide (i.e., method 1) in CCl_4 and CH_3CN, there was no measurable difference either in the intensity of the visible absorption immediately after the laser pulse or in the position of λ_{max}. However, the ratios of the visible to UV absorption intensities, monitored at 485 and 320 nm,[19] respectively, were slightly dependent on the solvent with $\Delta OD_{485}/\Delta OD_{320}$ varying

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[12] Russell, G. A. *J. Am. Chem. Soc.* **1957**, *79*, 2977–2978. Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 4897–4996. Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 4997–5001. Walling, C.; Mayahi, M. F. *J. Am. Chem. Soc.* **1959**, *81*, 1485–1489.

[13] For a review, see: Ingold, K. U.; Lusztyk, J.; Raner, K. D. *Acc. Chem. Res.* **1990**, *23*, 219–225.

[14] Raner, K. D.; Lusztyk, J.; Ingold, K. U. *J. Phys. Chem.* **1989**, *93*, 564–570 and references cited therein.

[15] O'Neill, P.; Steenken, S.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1975**, *79*, 2773–2776.

[16] The rate constant for H-atom abstraction from 1,3,5-trimethoxybenzene by cumyloxyl radicals was measured and found to be 5.2×10^5 M^{-1} s^{-1}. The pseudo-first-order rate constant with 0.6 M trimethoxybenzene is therefore $0.6 \times 5.2 \times 10^5$ s^{-1} = 3.1×10^5 s^{-1}.

[17] Avila, D. V.; Brown, C. E.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1993**, *115*, 466–470.

[18] Baignée, A.; Howard, J. A.; Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 6120–6123.

from a high of 1.35 in CCl_4 to a low of 0.72 in CH_3CN. Immediately after LFP, the absolute intensities of the visible and UV absorptions showed a linear dependence on laser flux, which implies that the transient(s) responsible for the two absorptions is (are) formed by a monophotonic process(es).[20] It is also worth noting that the growing in of the visible absorption was "instantaneous" even on the picosecond time scale, i.e., <50 ps (method 1 in CH_3CN), which lends further credence to the assignment of this absorption to the cumyloxyl radical.

The lifetimes of the species responsible for the visible and UV absorptions were equal (within experimental error) in a variety of solvents.[21] This proves that the two absorptions arise from a common transient,[22] i.e., the cumyloxyl radical. The intensities and rates of decay of the visible and UV absorptions were unaffected by oxygen as would be expected for a *tert*-alkoxyl radical,[23] though not for a *secondary* or *primary* alkoxyl (vide infra).

The extinction coefficient of the visible cumyloxyl absorption was measured in a pair of carefully matched experiments (method 1, 0.126 M peroxide in CH_3CN, 308 nm LFP). In one experiment, 1.0 M diphenylmethanol was added, this concentration being sufficient to capture 92% of the cumyloxyl radicals within 110 ns with the consequent generation of the benzophenone ketyl radical, for which $\epsilon_{545} = 3220\ M^{-1}\ cm^{-1}$).[25] From the ratio of the absorption intensities at 485 nm in the absence and 545 nm in the presence of the diphenylmethanol (appropriately corrected for the small absorption of the alcohol at the excitation wavelength) we estimate that $\epsilon_{485} \approx 1300\ M^{-1}\ cm^{-1}$ for cumyloxyl (see Table 1).

Radicals which have reasonably strong absorptions can often be photobleached by irradiation of these bands in a two-laser, two-color experiment.[26] The first laser pulse (generally at 266 or 308 nm) is used to synthesize the radicals, and shortly thereafter (i.e., before the radicals have decayed completely) a second laser operating at longer wavelengths is used to irradiate the visible absorption. By this procedure, the (4-methoxybenzoyl)oxyl radical[24a] and the (propyloxycarbonyl)oxyl radical[27] have been photobleached with decarboxylation to form the 4-methoxyphenyl and propyloxyl radicals, respectively, and the α,α-dimethoxybenzyl radical has been photobleached with loss of methyl radical and formation of methyl benzoate.[28] Applying this same procedure to cumyloxyl radicals gave a disappointing, and surprising, result: nothing happened!

Cumyloxyl radicals were synthesized by 308 nm LFP (method 1 in CH_3CN) and were then subjected to 532 nm LFP, the cumyloxyl radical's absorption at 532 nm being roughly half as intense as at its λ_{max} of 485 nm. Following this second laser pulse there was no bleaching at 485 nm nor at 320 nm nor was there any discernible change in the kinetics of decay at these two wavelengths. Cumyloxyl radicals generated in the same way in CH_3CN were also subjected to irradiation by a second laser right at their visible region absorption maximum, but even this did not change the intensities or decay kinetics monitored at 500 and 320 nm. A third, more vigorous experiment was therefore carried out. Cumyloxyl radicals were synthesized by 266 nm LFP in CH_3CN and were then irradiated with a second laser at 308 nm,[29] i.e., in their UV absorption band. Again, there was no bleaching at 320 nm nor at 485 nm. Indeed, there was a small increase in the OD at these two wavelengths owing to the generation of additional cumyloxyl radicals by the second, 308 nm laser pulse. The decay kinetics at 320 and 485 nm were also not affected by the 308 nm laser.

$$C_6H_5C(CH_3)_2O^\bullet \overset{h\nu}{\underset{\text{532, 485, or 308 nm}}{\not\longrightarrow}} C_6H_5COCH_3 + CH_3^\bullet$$

Our inability to photobleach cumyloxyl radicals is particularly surprising in view of the recent report of Banks and Scaiano that extremely high intensity 308 nm irradiation of cumyloxyl radicals actually does induce a photoassisted β-scission to acetophenone and methyl.[30] These workers utilized their new laser drop method, which encourages multiphoton chemistry during a laser pulse, i.e., the synthesis laser and the second laser are combined. The acetophenone/cumyl alcohol ratio was 46:54 upon 308 nm LFP of dicumyl peroxide in methanol by the laser drop method vs <2:>98 for 300 nm irradiation of a similar solution with a Rayonet lamp. Obviously, exciting the electronic transitions responsible for both the visible and the UV absorption is a very inefficient method for enhancing the rate of β-scission of cumyloxyl radicals, which means that the quantum yields for the photoinduced β-scission reaction must be very low.

(4-Methylcumyl)oxyl and (4-methoxycumyl)oxyl radicals were generated by method 3 using 266 nm LFP and CH_3CN as solvent. In both cases, transients are produced "instantaneously" which possess both a UV and a visible absorption. Relative to the λ_{max} for cumyloxyl, the λ_{max} for (4-methylcumyl)oxyl is shifted 25 nm into the red, while that for (4-methoxycumyl)oxyl[8] is shifted in the same direction by a dramatic 105 nm (see Table 1). The extinction coefficients of the visible absorptions at their λ_{max} increase somewhat along the series cumyloxyl, (4-methylcumyl)oxyl, and (4-methoxycumyl)oxyl (Table 1). The extinction coefficients for the two ring-substituted radicals were obtained in matched experiments using cumyloxyl as an actinometer, the implicit assumption being that the three hyponitrites (at 0.30 OD) have the same quantum efficiencies for alkoxyl radical production at 266 nm in CH_3CN.

Benzyloxyl,[8] (4-methylbenzyl)oxyl, and (4-methoxybenzyl)oxyl radicals were generated by direct 308 nm LFP of their parent hyponitrites (method 3). Transient absorptions in the visible and UV regions of the spectrum were formed "instantaneously". The benzyloxyl radical was also generated by 266 nm LFP of its parent hyponitrite (method 3) and by the photosensitized decomposition of the same precursor (method

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[19] It was not possible to determine the UV λ_{max} for any alkoxyl radical. Measurements at 320 nm correspond to ΔOD on the (steep) "side" of the UV absorption. The change in the 485/320 nm absorption intensity ratios may therefore be due either to solvent effects on the relative intensities of the two absorption bands or to a shift in the λ_{max} for the UV absorbance.

[20] Lachish, U.; Shafferman, A.; Stein, G. *J. Phys. Chem.* **1976**, *64*, 4205–4211.

[21] Solvent and lifetimes monitored at 485 and 320 nm in μs: CCl_4, 2.89 and 2.94; C_6H_6, 2.06 and 2.00; C_6H_5Cl, 2.42 and 2.44; Me_3COH, 0.90 and 0.97; CH_3CN, 1.33 and 1.34; $CH_3C(O)OH$, 0.46 and 0.48.

[22] Or, less probably, from two species in rapid equilibrium.

[23] This result rules out any possibility that (either of) the two absorptions could be due to a carbon-centered radical or to an excited triplet species.[24]

[24] (a) Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2877–2885. (b) Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2886–2893.

[25] Land, E. J. *Proc. R. Soc. London Ser. A* **1968**, *305*, 457–471.

[26] For reviews of two-laser and/or two-photon chemistry, i.e., the photochemistry of reaction intermediates, see: Scaiano, J. C.; Johnston, L. J. *Pure Appl. Chem.* **1986**, *58*, 1273–1278. Scaiano, J. C.; Johnston, L. J.; McGimpsey, W. G.; Weir, D. G. *Acc. Chem. Res.* **1988**, *21*, 22–29. Scaiano, J. C.; Johnston, L. J. *Org. Photochem.* **1989**, *10*, 309–355.

[27] Chateauneuf, J.; Lusztyk, J.; Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 6727–6731.

[28] Banks, J. T.; Scaiano, J. C.; Adam, W.; Oestrich, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 2473–2477.

[29] Using the 266/308 nm system with di-*tert*-butyl peroxide we were also unable to observe any photobleaching of the *tert*-butoxyl radical at 320 nm.

[30] Banks, J. T.; Scaiano, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 6409–6413.

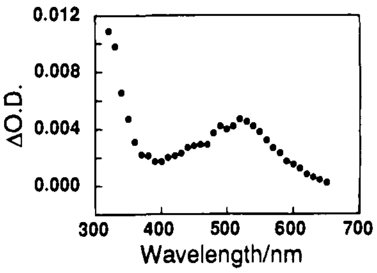


Figure 2. Transient absorption spectrum of the Tetralin-1-oxyl radical measured 0.35 μs after 266 nm LFP of 1.17 × 10^{-3} M 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide in CH_3CN.

5). The same tests which were used to assign the visible and UV absorptions to the cumyloxyl radical were applied to the transient absorptions obtained by LFP of dibenzyl hyponitrite. These tests indicated that both absorptions were due to the benzyloxyl radical. Indeed, the only test which gave a different result was the effect of oxygen, which, not entirely unexpectedly,[31] was found to react quite rapidly with the *primary* benzyloxyl radical,

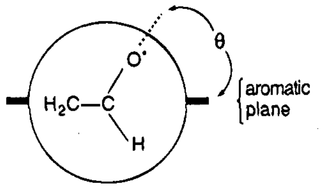
$$C_6H_5CH_2O^\bullet + O_2 \rightarrow C_6H_5CHO + HOO^\bullet$$

though it is inert toward the *tertiary* cumyloxyl radical.

The λ_{max} for benzyloxyl's visible absorption is blue-shifted by ca. 25 nm relative to cumyloxyl, but its extinction coefficient (measured as described above for the substituted cumyloxyl radicals) was found to be the same as that for cumyloxyl (see Table 1). The two 4-substituted benzyloxyl radicals show λ_{max} red-shifts relative to benzyloxyl just as were found in the cumyloxyl series. Indeed, the magnitudes of the red-shift produced by the two 4-substituents are essentially the same for the cumyloxyl and benzyloxyl series, viz., 25−30 nm for a 4-methyl substituent and 100−105 nm for a 4-methoxy substituent (see Table 1).

Tetralin-1-oxyl and indan-1-oxyl radicals were generated by method 2 in CH_3CN (266 nm LFP, ca. 0.08 M alkyl *tert*-butyl peroxide, 0.30 OD) and in CCl_4 (308 nm LFP, ca. 0.045 M peroxide, 0.30 OD). Tetralin-1-oxyl was also generated by 266 nm LFP of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide (method 4) in CH_3CN. Both radicals had absorptions in the visible region, and the λ_{max} values were unaffected by changes in the solvent. The λ_{max} values for Tetralin-1-oxyl (the spectrum of which is shown in Figure 2) and indan-1-oxyl are rather similar (520 and 530 nm, respectively) and are noticeably red-shifted relative to cumyloxyl and benzyloxyl (see Table 1). There was a UV absorption in the method 2 experiments, but of course, this could have been entirely due to the *tert*-butoxyl radical. It was for this reason that method 4 was employed. The ratios of the intensities of absorptions at 520 and 320 nm for Tetralin-1-oxyl were essentially identical in the method 4 (0.55:1) experiment as in the method 2 (0.68:1) experiment. It would appear that Tetralin-1-oxyl has a stronger absorption at 320 nm than does *tert*-butoxyl.

These two cyclic alkoxyl radicals were studied in order to discover whether "locking" the orientation of the C−O• bond with respect to the aromatic ring would have any profound effect on their visible absorption bands relative to the visible absorption bands of the "free-to-rotate" (in principle) benzyloxyl and cumyloxyl radicals. The energy-minimized structures for benzyloxyl and cumyloxyl were calculated by the AM1 method,[32] and the dihedral angles, θ, between the C−O• bond and the plane of the aromatic ring were found to be 0° for both of these radicals. Similar calculations were carried out on Tetralin-1-oxyl and indan-1-oxyl. For Tetralin-1-oxyl the nonaromatic ring adopts a half-chair conformation, and in the minimum energy structure the oxygen atom takes up a pseudoequatorial position with θ = 33°. However, the structure with the oxygen atom in the pseudoaxial position (which has θ = 61.5°) is only 0.9 kcal/mol higher in energy.[33] Thus, at ambient temperatures there will be ca. 82% of the pseudoequatorial conformer of Tetralin-1-oxyl and ca. 18% of the pseudoaxial conformer present. For indan-1-oxyl the 5-membered ring was found to be nonplanar, and in this radical also, the oxygen atom prefers the more equatorial-like position with θ = 51°. Thus, our experimental results (Table 1) suggest that "locking" the C−O• bond (mainly) at an angle of ca. 33° or ca. 51° with respect to the aromatic plane does not have any dramatic effect on the visible absorption relative to those for the θ = 0° benzyloxyl radical (the θ = 90° benzyloxyl was calculated to be a transition state which was 3.6 kcal/mol higher in energy, vide infra) and the θ = 0° cumyloxyl radical (for which the θ = 90° conformer would be even more strongly disfavored for steric reasons). The fact that the λ_{max} values for these two cyclic alkoxyl radicals are red-shifted relative to benzyloxyl and cumyloxyl is, we suggest, most simply explained as being largely, or entirely, due to an *o*-alkyl substituent effect. That is, the presence of the saturated ring necessarily means that both of these cyclic alkoxyl radicals have an alkyl group *ortho* to the carbon bearing the oxygen atom. By analogy with the red-shift of λ_{max} induced by *p*-methyl substitution (see Table 1), *o*-alkyl substitution should also be expected to induce a red-shift, just as is observed.



Diphenylmethoxyl radicals were generated by methods 1−4 using 266 nm LFP and CH_3CN as solvent. A visible absorption with λ_{max} = 530 nm and a UV absorption (monitored at 320 nm) appeared "instantaneously" with all four methods. This radical reacts with oxygen, but in the absence of oxygen has a lifetime of ~1500 ns, which is comparable to the lifetimes found for benzyloxyl (2300 ns) and cumyloxyl (1300 ns) under similar conditions. The diphenylmethoxyl radical reacts with cyclohexane with $k = (1.01 \pm 0.25) \times 10^6$ M^{-1} s^{-1} at 25 °C; i.e., within experimental error it shows the same reactivity toward cyclohexane as cumyloxyl[17] and *tert*-butoxyl[18] (vide supra).

1,1-Diphenylethoxyl radicals were generated in CH_3CN by methods 1 and 2 (266 nm LFP). A visible absorption with λ_{max} = 535 nm and a UV absorption (which was monitored at 320 nm) appeared "instantaneously". Under 760 Torr of O_2 both absorption bands decayed with lifetimes of 310 ns. This result

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[31] There is extensive evidence from gas phase studies for analogous reactions of O_2 with *primary* and *secondary* (but not *tertiary*) alkoxyl radicals with rate constants at room temperature reported to be in the range $3 \times 10^5 - 1 \times 10^7$ M^{-1} s^{-1}; see, e.g.: Barker, J. R.; Benson, S. W.; Golden, D. M. *Int. J. Chem. Kinet.* **1977**, *9*, 31−53. Batt, L.; Robinson, G. N. *Int. J. Chem. Kin.* **1979**, *11*, 1045−1053. Balla, R. J.; Nelson, H. H.; McDonald, J. R. *Chem. Phys.* **1985**, *99*, 323−335. Hartmann, D.; Karthäuser, J.; Sawyersyn, J. P. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 639−645.

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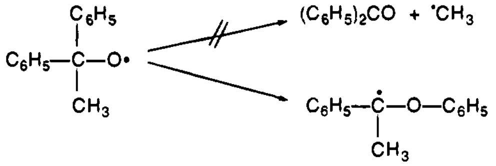
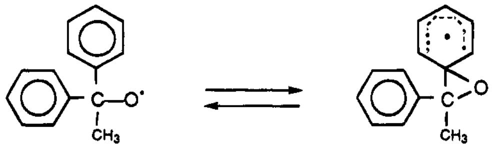
[33] An X-ray examination of a crystal of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide showed that the OOH group is in the pseudoaxial position with θ = 68.5°. It should be noted that the half-boat conformation of Tetralin-1-oxyl was calculated to be ca. 3.3 kcal/mol higher in energy than the ground state structure.

is in excellent agreement with a lifetime of 312 ns under nitrogen reported for the 535 nm absorption by Schuster and co-workers[9a] using method 2 (266 nm LFP, CH_3CN). We also found the decay of the 535 nm band to be the same under nitrogen as under oxygen. However, under nitrogen the 320 nm absorption shows first-order growth (lifetime 310 ns) following its "instantaneous" appearance after the laser pulse. We attribute this growth to stronger absorption at 320 nm of the 1-phenoxy-1-phenylethyl radical compared with the 1,1-diphenylethoxyl radical since it is well established that the latter does not undergo a β-scission reaction but, instead, rearranges with a carbon-to-oxygen migration of a phenyl group.[34]



The visible and UV absorptions which we assign to the 1,1-diphenylethoxyl radical were used to measure the rate constant for H-atom abstraction from cyclohexane by this radical under 760 Torr of O_2: $k(535\ \text{nm}) = (1.29 \pm 0.28) \times 10^6\ M^{-1}\ s^{-1}$ and $k(320\ \text{nm}) = (1.22 \pm 0.25) \times 10^6\ M^{-1}\ s^{-1}$. These two measurements serve to confirm that both the visible and the UV absorptions are due to the 1,1-diphenylethoxyl radical since they are equal (within experimental error) to the rate constants found for the reactions of other alkoxyl radicals with cyclohexane (vide supra).[17,18] We emphasize this point because Schuster and co-workers[9a] have previously assigned the 535 nm absorption to a 1-oxospiro[2.5]octadienyl radical which was assumed to be in rapid equilibrium with the 1,1-diphenylethoxyl radical.



Our work has demonstrated that it is not necessary to postulate the existence of a spirooctadienyl radical since (arylcarbinyl)oxyl radicals which do not rearrange have analogous absorptions in the visible region. Furthermore, cyclohexadienyl radicals (like other carbon-centered radicals) are known to react rapidly with oxygen,[35,36] but the 535 nm transient is inert toward oxygen. We therefore assign all the visible absorption bands discussed above to radicals having the (arylcarbinyl)oxyl structure. This assignment is supported by theoretical calculations (vide infra).

Theoretical Calculations

The molecular structures of benzyloxyl, cumyloxyl, four 4-substituted cumyloxyls, 2-phenylethyl, phenoxymethyl, and the cumylaminyl radical were optimized by the AM1 method[32] with the Gaussian 90 program.[37] For the six alkoxyl radicals, the molecular symmetry was constrained to the C_s point group (i.e., to structures with a plane of symmetry). In this way, the two close-lying electronic configurations with the unpaired electron localized mainly in one of the two lone-pair orbitals on oxygen (which are primarily of pπ-character) are orthogonal by symmetry and do not interact with one another. The Hartree-Fock approximation is, therefore, adequate to describe the ground states of these radicals. If the plane of symmetry is removed, the use of a single-configuration wave function may not suffice to describe the electronic wave function. For all the alkoxyl radicals the ground electronic state was found to be of A″ symmetry. The unpaired electron is largely localized in the oxygen lone pair orbital which is perpendicular to the plane of the aromatic ring. The 2-phenylethyl and phenoxymethyl radicals were fully optimized, and the cumylaminyl radical was treated in the same way as the alkoxyl radicals. For all nine radicals the C−C bond lengths in their aromatic rings were found to be very similar to the C−C bond length in benzene. The bond lengths between the atom bearing the unpaired electron and the atom joining it to the aromatic ring were found to be roughly intermediate between the lengths of a single and a double bond. These calculated bond lengths are available as supplementary material.

INDO/S[38] plus CI calculations were performed to calculate the excitation energies.[39] The CI scheme was based on Rumer diagrams[43] and was limited to singly excited configurations from the ground state wave function. For the six alkoxyl radicals, the two configurations with the unpaired electron in each of the lone pair orbitals on oxygen were taken as the starting wave function. This effectively amounts to the introduction of some doubly excited configurations.

The benzyloxyl radical was also optimized by the ROHF/3-21G method with the C−O• bond coplanar with the aromatic ring ($\theta = 0°$) and perpendicular to the ring plane ($\theta = 90°$). Force field calculations showed that the coplanar configuration (lowest frequency = 60 cm^{-1}) was more stable by 3.6 kcal/mol than the perpendicular configuration which was actually a transition state with one imaginary frequency (98i cm^{-1}). Similar calculations on the cumyloxyl radical showed that the minimum on the potential energy surface with the lowest vibrational frequency (49 cm^{-1}) also had the C−O• bond coplanar with the aromatic ring.

The effects on the calculated excitation energies of rotation about the $C_6H_5-CH_2O^\bullet$ bond and of elongation of the C_6H_5-$CH_2-O^\bullet$ bond produced only minor changes in the overall

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Table 2. INDO/S+CI $D_0 \rightarrow D_n$ Excitation Energies and $D_0 \rightarrow D_n$ Oscillator Strengths[a]

	excitation energy, nm (oscillator strength × 10^4)					
radical	D_1	D_2	D_3	D_4	D_5	D_6
$C_6H_5CH_2O^\bullet$ [b]	3099 (1)	435 (36)	344 (222)[c]	326 (0)	318 (44)	298 (31)
$C_6H_5C(CH_3)_2O^\bullet$ [b]	2115 (2)	432 (39)[d]	343 (177)[c]	318 (21)	298 (33)	286 (9)
$4\text{-}NCC_6H_4C(CH_3)_2O^\bullet$ [b]	1235 (0)	409 (38)[d]	319 (109)[e]	311 (164)[d]	297 (153)[e]	277 (17)
$4\text{-}CF_3C_6H_4C(CH_3)_2O^\bullet$ [b]	1805 (2)	421 (23)	320 (95)[e]	310 (57)[d]	296 (99)[e]	292 (0)
$4\text{-}CH_3C_6H_4C(CH_3)_2O^\bullet$ [b]	2513 (1)	447 (114)[d]	353 (147)[e]	322 (10)	311 (0)	295 (10)
$4\text{-}CH_3OC_6H_4C(CH_3)_2O^\bullet$ [b]	10142 (0)	511 (418)[d]	373 (0)	348 (9)	315 (0)	288 (0)
$C_6H_5CH_2CH_2^\bullet$ [f,g]	419 (0)	307 (0)	303 (0)	265 (52)	261 (0)	249 (100)
$C_6H_5OCH_2^\bullet$ [f]	418 (1)	326 (3)	306 (3)	268 (165)	259 (6)	254 (432)
$C_6H_5C(CH_3)_2NH^\bullet$ [g,h]	446 (19)	414 (0)	310 (0)	305 (0)	266 (41)	264 (6)

[a] Full details are available as supplementary material. [b] The states and $D_0 \rightarrow D_n$ transitions are as follows: $D_0(A'')$; $D_1(A')$ (n_O); $D_2(A'')$ ($\pi \rightarrow \pi^*$); $D_3(A'')$ ($\pi \rightarrow \pi^*$); $D_4(A')$ ($n_O \rightarrow \pi^*$); $D_5(A'')$ ($\pi \rightarrow \pi^*$); $D_6(A'')$ ($\pi \rightarrow \pi^*$), except $4\text{-}CF_3C_6H_4C(CH_3)_2O^\bullet$, $D_0 \rightarrow D_6(A'')$ ($n_O \rightarrow \pi^*$); $4\text{-}CH_3C_6H_4C(CH_3)_2O^\bullet$, $D_0 \rightarrow D_5(A')$ ($n_O \rightarrow \pi^*$); and $4\text{-}CH_3OC_6H_4C(CH_3)_2O^\bullet$, $D_0 \rightarrow D_5$ and $D_0 \rightarrow D_6(A')$ ($n_O \rightarrow \pi^*$). [c] $D_1 \rightarrow D_n$ oscillator strength (OS) 3×10^{-4}. [d] $D_1 \rightarrow D_n$ OS 1×10^{-4}. [e] $D_1 \rightarrow D_n$ OS 2×10^{-4}. [f] All the $D_0 \rightarrow D_n$ transitions are ($\pi \rightarrow \pi^*$). [g] No visible absorption was detected when this radical was generated by LFP. [h] The $D_0 \rightarrow D_n$ transitions are as follows: D_1 ($n_N \rightarrow \pi_N$); D_2 to D_6 ($\pi \rightarrow \pi^*$).

pattern of the electronic transitions. Most noteworthy was an increase by some 1400 cm^{-1} (ca. 4 kcal/mol) in the $D_0 \rightarrow D_1$ energy gap on going from the conformation with the $C-O^\bullet$ bond coplanar with the aromatic ring to the conformation with the $C-O^\bullet$ bond perpendicular to the ring plane.

The $D_0 \rightarrow D_n$ ($n = 1-6$) excitation energies and oscillator strengths for the eight radicals studied theoretically are given in Table 2, and the nature of the electronically excited states are indicated in the footnotes to this table. (Full details for n up to 19 for the alkoxyl radicals, n up to 11 for the two carbon-centered radicals, and n up to 12 for the aminyl radical are available as supplementary material.)

Discussion

In contrast to benzyloxyl and related radicals the *tert*-butoxyl radical itself does not, possess an absorption in the visible region. However, a weak absorption in the visible (440 nm) is induced in the presence of 1,3,5-trimethoxybenzene. We attribute this absorption to a charge transfer band involving a π-complex between the radical and this very electron-rich aromatic. It is possible that this is only a very weak complex which "ties up" only a minor fraction of the *tert*-butoxyl radicals since this would provide a simple explanation for the fact that the rate constant for *tert*-butoxyl attack on cyclohexane was essentially unchanged by the addition of 0.6 M trimethoxybenzene.

A comparison of the visible absorption bands for benzyloxyl and cumyloxyl radicals and similarly substituted benzyloxyl and cumyloxyl radicals (Table 1) shows that substitution of the two α-hydrogen atoms with two methyl groups has only a minor effect on λ_{max} ($\Delta\lambda_{max} = 20-30$ nm) and no effect on ϵ. These results are mirrored by our theoretical calculations which indicate that the visible absorption arises from the $D_0(A'') \rightarrow D_2(A'')$ ($\pi \rightarrow \pi^*$) transition (Table 2). This transition produces an increase in the electron density on the oxygen atom. For benzyloxyl a Mulliken population analysis yields a negative charge on oxygen of -0.26 in the D_0 ground state which rises to -0.45 in the D_2 state (and -0.95 in D_3). However, this increase in the negative charge on the oxygen atom is not brought about by the dominant (82%) contribution to the CI wave function. The dominant configuration in this wave function arises from transfer of an electron from the HOMO (to which the oxygen's $2p_z$ contribution is 0.20) to the LUMO (in which the contribution of the O $2p_z$ orbital is below 0.01). Thus, the dominant contribution actually produces a slight decrease in the negative charge on the oxygen atom. However, there is also a contribution (18%) to this wave function from a HOMO → SOMO transition (with a 0.94 contribution to the SOMO from the O $2p_z$ orbital). This obviously increases the electronic charge on the oxygen atom, and it is this which plays the dominant role in charge flow *to* oxygen.[44] It should be noted that INDO/S is not expected to provide quantitative excitation energies in precise agreement with experiment. What it does provide is an explanation for the origin of visible absorption in (arylcarbinyl)oxyl radicals, and it also can be used to assess whether or not a substituent is likely to produce a redistribution of oscillator strengths and a significant shift in the band maximum. Thus, for the benzyloxyl/cumyloxyl pair the measured λ_{max} are 460/485 nm and have the same extinction coefficients, while the calculated $D_0 \rightarrow D_2$ transition energies are 435/432 nm with very similar oscillator strengths (0.0036/0.0039).

The relatively small effect of α-substitution is further emphasized by the very similar λ_{max} values found for diphenylmethoxyl (530 nm) and diphenylethoxyl (535 nm). Indeed, even the replacement of a methyl group in cumyloxyl by a phenyl group only increases λ_{max} by $535 - 485 = 50$ nm.

By way of contrast, ring substitution can have a fairly dramatic effect on λ_{max}. Furthermore, the direction in which a *para* ring substituent shifts λ_{max} and even the magnitude of the shift are nicely reflected by theory. For instance, for the cumyloxyl/(4-methoxycumyl)oxyl pair the measured λ_{max} values of 485/590 nm show a substituent-induced shift, $\Delta\lambda_{max} = 105$ nm, while the corresponding calculated $D_0 \rightarrow D_2$ transition energies are 432/511 nm, a difference of 79 nm. However, it should be noted that the calculations grossly overestimate the difference in the band intensities for the cumyloxyl/(4-methoxycumyl)oxyl pair with transition moments of 0.0039/0.0418, whereas the measured extinction coefficients are very similar, viz., 1300/1550 M^{-1} cm^{-1}.

The calculations indicate that electron-withdrawing substituents produce a blue-shift in λ_{max}, and electron-donating substituents a red-shift. Indeed, the order in which the calculated $D_0 \rightarrow D_2$ transition wavelengths increase for the 4-substituted cumyloxyl radicals (viz., $CN < CF_3 < H < CH_3 < CH_3O$) parallels the polar effects of the substituents. This implies that there would probably be a "reasonable" Hammett-type correlation between the experimentally measured energies at the visible absorption maxima (which will be proportional to $1/\lambda_{max}$) and σ^+ substituent constants. An attempt was made to explore this idea experimentally beyond the unsubstituted and the 4-CH_3- and 4-CH_3O-substituted cumyloxyl radicals, but unfortunately

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(44) The situation with regard to the D_3 state is similar with the largest (67%) contribution to the wave function being a HOMO → LUMO transition with little charge flow. However, other minor contributions to the D_3 wave function involve transitions from the occupied π orbitals to the SOMO, which produces a large net increase in the negative charge on the oxygen.

we failed in our attempts to synthesize the 4-cyano- and the (4-trifluoromethyl)cumyl hyponitrites.

The experimental measurements demonstrate that there is no gross change in the position of the visible absorption band nor any major change in its intensity as the calculated dihedral angle, θ, between the $C-O^\bullet$ bond and the plane of the aromatic ring is increased from ~0° (benzyloxyl, cumyloxyl) to (mainly, vide supra) ~33° (Tetralin-1-oxyl) and to ~51° (indan-1-oxyl). The calculations on the benzyloxyl radical are in agreement with these experimental observations in that there was no gross change in the $D_0 \rightarrow D_2$ transition wavelengths between the energy minimum configuration ($\theta = 0°$) and the $\theta = 90°$ transition state. As noted above, the unpaired electron is largely localized in the oxygen 2p orbital which is perpendicular to the plane of the aromatic ring, and this appears to hold true whatever the magnitude of θ.

Laser irradiation of the cumyloxyl radical at wavelengths in the visible and ultraviolet regions where it absorbs and laser irradiation of the *tert*-butoxyl radical in the UV where it absorbs produced no change in the concentrations of these radicals (see Results). Our inability to photobleach alkoxyl radicals implies a very low quantum efficiency for their photodissociation to a carbonyl compound and an alkyl radical (β-scission). We suggest that this is probably due to similar geometries for the excited and ground states of these radicals, at least insofar as their $C-CH_3$ bond lengths are concerned. The predominant mode of decay from the excited states is therefore a direct transition to the ground state rather than a C−C bond dissociation although the latter process does occur under very intense irradiation.[30]

Earlier experimental work on aroyloxyl radicals, $ArC(O)O^\bullet$,[24] arylperoxyl radicals, $ArOO^\bullet$,[45,46] and aroylcarbinyl radicals, $ArC(O)CH_2^\bullet \leftrightarrow ArC(O^\bullet)=CH_2$,[47,48] has shown that all of these radicals exhibit absorptions in the visible region of the spectrum, just as do the (arylcarbinyl)oxyl radicals. Our theoretical calculations (Table 2) also indicate that $ArXY^\bullet$ radicals will have an absorption band of reasonable intensity in the visible region only when Y is an oxygen atom. That is, neither $C_6H_5CH_2CH_2^\bullet$ nor $C_6H_5OCH_2^\bullet$ has electronic transitions in the visible region of the spectrum with significant oscillator strengths. The $C_6H_5C(CH_3)_2NH^\bullet$ radical does have a calculated $D_0 \rightarrow D_1$ electronic transition in the visible region at 446 nm, but the calculated oscillator strength is only about half that of the benzyloxyl or cumyloxyl radical.[49]

Experimental Section

Materials. Commercial solvents of the highest available purity were utilized since various experiments demonstrated that further purification had no effect on the spectral or kinetic properties of the radicals generated in this work: CH_3CN and CCl_4 (OmniSolve), C_6H_6 (Aldrich), C_6H_5Cl (BDH), $(CH_3)_3COH$ (Fisher Scientific), and $CH_3C(O)OH$ (Anachemia). 1,3,5-Trimethoxybenzene was purchased (Aldrich) and used as received. Di-*tert*-butyl peroxide (Aldrich) was passed through an alumina column before use. Di-α-cumyl peroxide (Aldrich) was recrystallized (3×) from methanol.

The following hyponitrites were synthesized by literature methods,[50-52] and their NMR spectra were recorded on a 200 MHz instrument in $CDCl_3$ unless otherwise noted. **Dicumyl hyponitrite:**[50] mp 75.5−76.5 °C (lit.[50] mp 75 °C); ^1H NMR δ 1.58 (s, 12H, $2C(CH_3)_2$), 7.06−7.90 (m, 10H, 2*Ar*). **Bis(4-methylcumyl) hyponitrite:**[50] mp 74 −75 °C (lit.[50] mp 76 °C); ^1H NMR δ 1.80 (s, 12H, $2C(CH_3)_2$), 2.45 (s, 6H $2ArCH_3$), 7.24 (d, 4H, 2*Ar*, J = 8.8 Hz), 7.36 (d, 4H, 2*Ar*, J = 8.8 Hz). **Bis(4-methoxycumyl) hyponitrite:**[50] mp 81−82 °C (lit.[50] mp 82 °C); ^1H NMR δ 1.69 (s, 12H, $2C(CH_3)_2$), 3.80 (s, 6H, $2OCH_3$), 6.84 (d, 4H, 2*Ar*, J = 8.0 Hz), 7.26 (d, 4H, 2*Ar*, J = 8.0 Hz). **Dibenzyl hyponitrite:**[51] mp 48 °C (lit.[51] mp 47−48 °C); ^1H NMR δ 5.26 (s, 4H, $2CH_2$), 7.44−7.49 (m, 10H, 2*Ar*). **Bis(4-methylbenzyl) hyponitrite:**[50] mp 73 °C; ^1H NMR δ 2.34 (s, 6H, $2CH_3$), 5.19 (s, 4H, $2CH_2$), 7.13−7.27 (m, 8H, 2*Ar*); ^{13}C NMR δ 21.19 (CH_3), 75.38 (CH_2), 128.73 (*Ar*), 129.20 (*Ar*), 132.63 (*Ar*), 138.31 (*Ar*). Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71. Found: C, 70.98; H, 6.53. **Bis(4-methoxybenzyl) hyponitrite:**[50] mp 69 °C; ^1H NMR δ 3.80 (s, 6H, $2OCH_3$), 5.17 (s, 4H, $2CH_2$), 6.85−6.90 (m, 4H, *Ar*), 7.27−7.31 (m, 4H, *Ar*); ^{13}C NMR δ 55.27 (CH_3), 75.28 (CH_2), 112.30 (*Ar*), 113.94 (*Ar*), 127.75 (*Ar*), 130.47 (*Ar*). Calcd for $C_{16}H_{18}N_2O_4$: C, 63.57; H, 6.00. Found: C, 63.52; H, 6.21. **Bis(diphenylmethyl) hyponitrite:**[52] mp 72 °C (lit.[52] mp 72 °C); ^1H NMR δ 6.42 (s, 2H, $2Ar_2CH$), 7.30−7.34 (m, 20H, $2Ar_2CH$).

The following peroxides and hydroperoxides were also synthesized by literature methods.[9a,53,54] ***tert*-Butyl 1,1-diphenylethyl peroxide:**[9a] mp 42−43 °C (lit.[9a] mp 42.1−43.5 °C); ^1H NMR δ 1.20 (s, 9H, $C(CH_3)_3$), 1.99 (s, 3H, CH_3), 7.23−7.36 (m, 20H, 2*Ar*). **Bis(diphenylmethyl) peroxide:**[53] mp 112 °C (lit.[53] mp 112−113 °C); ^1H NMR δ 6.08 (s, 2H, $2Ar_2CH$), 7.22−7.34 (m, 20H, $2Ar_2CH$); ^{13}C NMR δ 87.50 (Ar_2CHO), 127.89 (*Ar*), 128.24 (*Ar*, one coincidental chemical shift), 139.58 (*ipso C*). **Diphenylmethyl hydroperoxide:**[53] mp 49 °C (lit.[53] mp 48−50 °C); ^1H NMR δ 6.08 (s, 1H, Ar_2CH), 7.36−7.38 (m, 10H, Ar_2CH), 8.03 (s, 1H, OOH); ^{13}C NMR δ 89.49 ($COOH$), 127.58 (*Ar*), 128.32 (*para C*), 128.61 (*Ar*), 138.91 (*ipso C*). **1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide:**[54] mp 54 °C (lit.[54] mp 54.0−54.5 °C); ^1H NMR δ 1.72−1.90 (m, 6H, $3CH_2$), 5.03−5.07 (m, 1H, $ArCHO$), 7.11−7.44 (m, 4H, *Ar*), 7.71 (s, 1H, OOH).

***tert*-Butyl 1,1-diphenylmethyl peroxide**[55] was prepared by treating diphenylmethyl bromide and *tert*-butyl hydroperoxide in diethyl ether with silver trifluoroacetate following the general procedure of Cookson et al.:[56] mp 72.0−72.5 °C; ^1H NMR δ 1.24 (s, 9H, $C(CH_3)_3$), 5.96 (s, 1H, Ph_2CH), 7.30−7.34 (m, 10H, 2*Ar*); ^{13}C NMR (400 MHz, $CDCl_3$) δ 26.51 (CH_3), 80.51 ($C(CH_3)_3$), 87.29 (Ph_2CHO) 127.20, 127.62 (*ortho*, *meta*, and *para* aromatic *C*), 140.35 (*ipso C*).

1,2,3,4-Tetrahydro-1-naphthyl *tert*-butyl peroxide[57] was prepared from *tert*-butyl bromide and 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide using the procedure of Cookson et al.:[56] colorless liquid (40% yield after chromatography on SiO_2); ^1H NMR δ 1.26 (s, 9H, $C(CH_3)_3$), 1.71−1.81 (m, 2H, CH_2), 1.92−1.97 (m, 1H, CHH), 2.32−2.37 (m, 1H, CHH), 2.67−2.71 (m, 1H, CHH), 2.76−2.81 (m, 1H, CHH), 4.97 (m, 1H, CHO), 7.08−7.43 (m, 4H, *Ar*); ^{13}C NMR δ 18.04 ($ArCH_2$), 26.60 (CH_3), 27.03 ($ArCH_2CH_2$), 29.29 ($ArCH_2CH_2CH_2$), 78.72 ($ArC(H)O$), 79.96 ($C(CH_3)_3$), 125.55, 128.10, 128.97, 130.92 (all *Ar*), 133,36, 138.75 (both *ipso C*).

1-Indanyl *tert*-butyl peroxide[57] was prepared in a similar manner[56] using 1-indanyl hydroperoxide: colorless liquid (9% yield after chromatography on SiO_2); ^1H NMR δ 1.26 (s, 9H, $C(CH_3)_3$), 2.23−2.33 (m, 2H, CH_2), 2.77−2.88 (m, 1H, CHH), 3.02−3.14 (m, 1H, CHH), 5.45 (m, 1H, CHO), 7.18−7.28 (m, 3H, *Ar*), 7.47−7.50 (m, 1H, *Ar*).

Time-resolved laser flash photolysis was carried out in 7 mm × 7 mm static or flow cells at an absorbance of ca. 0.3 OD at the exciting laser wavelength. The apparatus and experimental procedures have been described in detail elsewhere.[58,59]

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Supplementary Material Available: Heavy atom AM1 optimized bond lengths for some of the radicals considered in this work (Table III) and INDO/S+CI $D_0 \rightarrow D_n$ excitation energies and $D_0 \rightarrow D_n$ and $D_1 \rightarrow D_n$ oscillator strengths for these same radicals (Tables IV–XII) (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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