J. Org. Chem. **2002,** *67,* 2266−2270

Spectral Properties and Absolute Rate Constants for *β*-Scission of Ring-Substituted Cumyloxyl Radicals. A Laser Flash Photolysis Study

Enrico Baciocchi,[1a] Massimo Bietti,*,[1b] Michela Salamone,[1b] and Steen Steenken[1c]

Dipartimento di Chimica, Università "La Sapienza", P.le A. Moro, 5 I-00185 Rome, Italy,
Dipartimento di Scienze e Tecnologie Chimiche, Università "Tor Vergata", Via della Ricerca Scientifica, 1
I-00133 Rome, Italy, and Max-Planck-Institut für Strahlenchemie, D-45413 Mülheim, Germany

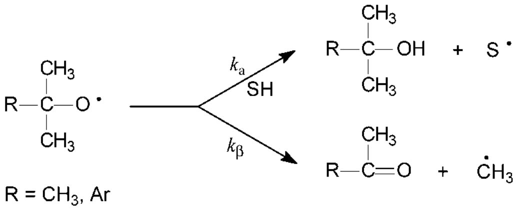
bietti@uniroma2.it.

Received November 21, 2001

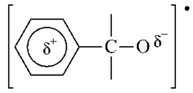
A laser flash photolysis study of the spectral properties and β-scission reactions of a series of ring-substituted cumyloxyl radicals has been carried out. All cumyloxyl radicals display a broad absorption band in the visible region of the spectrum, which decays on the microsecond time scale, leading to a strong increase in absorption in the UV region of the spectrum, which is attributed to the corresponding acetophenone formed after β-scission of the cumyloxyl radicals. The position of the visible absorption band is red-shifted by the presence of electron-donating ring substituents, while a blue-shift is observed in the presence of electron-withdrawing ring substituents, suggesting that + R ring substituents promote charge separation in the excited cumyloxyl radical through stabilization of the partial positive charge on the aromatic ring of an incipient radical zwitterion. Along this line, an excellent Hammett-type correlation between the experimentally measured energies at the visible absorption maxima of the cumyloxyl radicals and σ^+ substituent constants is obtained. A red-shift is also observed on going from MeCN to MeCN/H_2O for all cumyloxyl radicals, pointing toward a specific effect of water. The ring substitution does not influence to a significant extent the rate constants for β-scission of the cumyloxyl radicals, which varies between 7.1×10^5 and 1.1×10^6 s^{-1}, a result that suggests that cumyloxyl radical β-scission is not governed by the stability of the resulting acetophenone. Finally, k_β increases on going from MeCN to the more polar MeCN/H_2O 1:1 for all cumyloxyl radicals, an observation that reflects the increased stabilization of the transition state for β-scission through increased solvation of the incipient acetophenone product.

Alkoxyl radicals are important intermediates that play a major role in lipid peroxidation,[2] in the photooxidation of hydrocarbons in the atmosphere,[3] and in several autoxidation processes occurring in industrial and biological systems.[2] Among these radicals, *tert*-butoxyl and cumyloxyl have attracted considerable attention, and their reactivity, which is mainly related to hydrogen atom transfer and C−C β-scission reactions (Scheme 1), has been the subject of several studies.[4,5]

Scheme 1



A recent and important discovery was that arylcarbinyloxyl radicals display a broad absorption band in the visible region of the spectrum whose position is significantly red-shifted by the presence of electron-donating ring substituents,[6,7] an observation that led to the suggestion that such radicals are characterized by a certain degree of internal charge transfer, with the aromatic ring bearing a partial positive charge.



On the basis of theoretical calculations, the visible absorption band has been attributed to a $\pi \rightarrow \pi^*$ transi-

---

(1) (a) Universitá "La Sapienza". (b) Universitá "Tor Vergata". (c) Max-Planck-Institut.

(2) Halliwell, B.; Gutteridge, J. M. C. *Free Radicals in Biology and Medicine*, 3rd ed.; Oxford University Press: 1999.

(3) See for example: (a) Méreau, R.; Rayez, M.-T.; Caralp, F.; Rayez, J.-C. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3765−3772. (b) Fittschen, C.; Hippler, H.; Viskolcz, B. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1677−1683. (c) Atkinson, R. *Int. J. Chem. Kinet.* **1997**, *29*, 99−111.

(4) Leading references on the reactivity of *tert*-butoxyl radicals: (a) Weber, M.; Fischer, H. *J. Am. Chem. Soc.* **1999**, *121*, 7381−7388. (b) Tsentalovich, Y. P.; Kulik, L. V.; Gritsan, N. P.; Yurkovskaya, A. V. *J. Phys. Chem. A* **1998**, *102*, 7975−7980. (c) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520−4527. (d) Walling, C. *Pure Appl. Chem.* **1967**, *15*, 69−80.

(5) Leading references on the reactivity of cumyloxyl radicals: (a) Avila, D. V.; Ingold, K. U.; Lusztyk, J.; Green, W. H.; Procopio, D. R. *J. Am. Chem. Soc.* **1995**, *117*, 2929−2930. (b) Banks, J. T.; Scaiano, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 6409−6413. (c) Avila, D. V.; Brown, C. E.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1993**, *115*, 466−470. (d) Neville, A. G.; Brown, C. E.; Rayner, D. M.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1989**, *111*, 9269−9270. (e) Baignée, A.; Howard, J. A.; Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 6120−6123.

(6) Avila, D. V.; Ingold, K. U.; Di Nardo, A. A.; Zerbetto, F.; Zgierski, M. Z.; Lusztyk, J. *J. Am. Chem. Soc.* **1995**, *117*, 2711−2718.

(7) Avila, D. V.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 6576−6577.

10.1021/jo0163041 CCC: $22.00

tion, creating an increase in the electron density on the oxygen atom. On the basis of such calculations, it was also predicted that electron-withdrawing ring substituents should produce a blue-shift in the position of the visible absorption band, but no experimental evidence of this was provided.[6]

In this context, it seemed worthwhile to study the influence of both electron-releasing and electron-withdrawing ring substituents on the spectral properties of cumyloxyl radicals. Moreover, since the internal charge transfer discussed above might also influence the arylcarbinyloxyl radical ground-state energy, as well as that of the transition state for the β-scission reaction described in Scheme 1, a study of the influence of ring substitution upon the rate constant for β-scission of cumyloxyl radicals was also carried out.

Thus, in this paper we report on a laser flash photolysis study of the spectral properties and reactivities of ring-substituted cumyloxyl radicals.

Results

Cumyloxyl radicals ($ArC(CH_3)_2O^\bullet$) were generated at room temperature by 248 nm laser flash photolysis (LFP) of dicumyl peroxide or *tert*-butyl cumyl peroxides (between 1.1 and 5.5 × 10^{-3} M) bearing a variety of ring substituents ($ArC(CH_3)_2OOC(CH_3)_3$: Ar = 4-MeC_6H_4, 4-$MeOC_6H_4$, 3,4-$(MeO)_2C_6H_3$, 2,5-$(MeO)_2C_6H_3$, 3-ClC_6H_4, 4-ClC_6H_4, 4-$CF_3C_6H_4$), in MeCN and MeCN/H_2O (eqs 1 and 2, respectively).

$$C_6H_5C(CH_3)_2O{-}OC(CH_3)_2C_6H_5 \xrightarrow[248\ \text{nm}]{h\nu} 2C_6H_5C(CH_3)_2O^\bullet \quad (1)$$

$$ArC(CH_3)_2O{-}OC(CH_3)_3 \xrightarrow[248\ \text{nm}]{h\nu} ArC(CH_3)_2O^\bullet + (CH_3)_3CO^\bullet \quad (2)$$

However, 248 nm laser irradiation of 2,5-$(MeO)_2C_6H_3$-$C(CH_3)_2OOC(CH_3)_3$, both in MeCN and MeCN/H_2O, did not lead to the formation of the expected cumyloxyl radical 2,5-$(MeO)_2C_6H_3C(CH_3)_2O^\bullet$. A relatively long-lived transient was formed instead, showing absorption maxima around 310 and 455 nm, which was attributed to the aromatic radical cation[8] formed by photoionization of the parent peroxide. This assignment is supported by the observation that 248 nm irradiation of 2,5-dimethoxybenzyl alcohol in H_2O led to the simultaneous formation of the solvated electron and of a species characterized by absorption maxima at 310 and 455 nm, identical to those observed for 2,5-dimethoxybenzyl alcohol radical cation generated by pulse radiolysis in aqueous solution.[8]

All cumyloxyl radicals displayed a broad absorption band in the visible region of the spectrum, which is unaffected by oxygen.[6] This band was observed to decay on the microsecond time scale, leading in all cases to a corresponding strong increase in absorption in the UV region of the spectrum that, again, is unaffected by oxygen. For example, in the case of *tert*-butyl 3,4-dimethoxycumyl peroxide, the time-resolved spectra obtained after 248 nm LFP in MeCN (Figure 1) show after 0.13 μs (filled circles) an absorption band centered at 670 nm, which is attributed to the 3,4-dimethoxycumyloxyl radical.

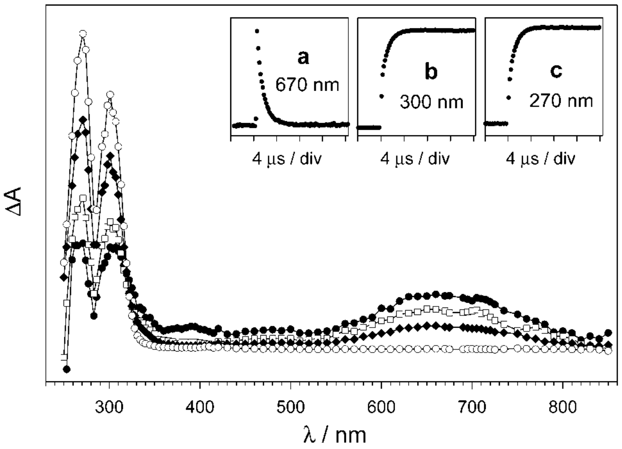


Figure 1. Time-resolved absorption spectra observed after 248 nm LFP of *tert*-butyl 3,4-dimethoxycumyl peroxide (1.1 mM) in an Ar-saturated MeCN solution at 0.13 μs (filled circles), 0.38 μs (empty squares), 1 μs (filled diamonds), and 7 μs (empty circles) after the 20 ns, 40 mJ laser flash. Insets: (a) First-order decay of the 3,4-dimethoxycumyloxyl radical monitored at 670 nm and (b and c) the corresponding first-order buildup of absorption at 270 and 300 nm, respectively, due to the formation of 3,4-dimethoxyacetophenone.

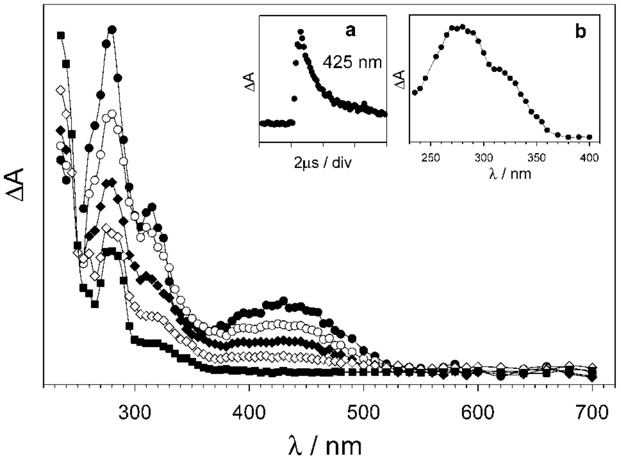


Figure 2. Time-resolved absorption spectra observed after 248 nm LFP of *tert*-butyl 4-trifluoromethylcumyl peroxide (5.5 mM) in an Ar-saturated MeCN solution at 55 (filled circles), 150 (empty circles), 350 (filled diamonds), 1500 (empty diamonds) and 7000 ns (filled squares) after the 20 ns, 40 mJ laser flash. Insets: (a) First-order decay of the 4-trifluoromethylcumyloxyl radical monitored at 425 nm and (b) time-resolved absorption spectra observed after 248 nm LFP of di-*tert*-butyl peroxide (150 mM) in an Ar-saturated MeCN solution at 75 ns (filled circles), after the 20 ns, 40 mJ laser flash.

This species undergoes a first-order decay (inset a) that is accompanied by a simultaneous buildup of optical density at 300 and 270 nm (insets b and c, respectively), assigned to 3,4-dimethoxyacetophenone, which shows two absorption maxima at these wavelengths.

Figure 2 displays the time-resolved spectra obtained after 248 nm LFP of *tert*-butyl 4-trifluoromethylcumyl peroxide in MeCN. The spectrum recorded after 55 ns (filled circles) shows a broad absorption band in the visible (around 425 nm), which is assigned to the 4-trifluoromethylcumyloxyl radical, an intense band centered

---

[8] Baciocchi, E.; Bietti, M.; Gerini, M. F.; Manduchi, L.; Salamone, M.; Steenken, S. *Chem. Eur. J.* **2001**, *7*, 1408−1416.

Table 1. Visible Absorption Band Maximum Wavelengths for the Cumyloxyl Radicals ($ArC(CH_3)_2O^{\bullet}$) and Kinetic Data for Their Decay and the Buildup of the Product Acetophenone in MeCN and MeCN/H_2O

Ar	solvent	λ_{max} (vis)/nm[a]	$k_{\uparrow}/s^{-1}$ [b]	$k_{\downarrow}/s^{-1}$ [c]
4-$CF_3C_6H_4$	MeCN	425		1.1×10^6
	MeCN/H_2O[d]	445		2.4×10^6
3-ClC_6H_4	MeCN	445		1.0×10^6
	MeCN/H_2O[d]	480	2.0×10^6	1.8×10^6
C_6H_5	MeCN	485	7.0×10^5	7.8×10^5
	MeCN/H_2O[d]	515	2.7×10^6	2.7×10^6
4-ClC_6H_4	MeCN	500	1.1×10^6	1.0×10^6
	MeCN/H_2O[d]	530	3.6×10^6	3.1×10^6
4-MeC_6H_4	MeCN	510	7.2×10^5	7.1×10^5
	MeCN/H_2O[d]	555	2.8×10^6	2.8×10^6
4-$MeOC_6H_4$	MeCN	580	1.1×10^6	1.0×10^6
	MeCN/H_2O[d]	625	3.6×10^6	3.2×10^6
3,4-$(MeO)_2C_6H_3$	MeCN	670	9.9×10^5	9.7×10^5
	MeCN/H_2O[e]	690	-	2.1×10^6

[a] Visible absorption maximum of the cumyloxyl radical. [b] Determined by following the buildup of the pertinent acetophenone between 240 and 300 nm. Error ≤10%. [c] Determined by following the decay of the cumyloxyl radical at the visible absorption maximum. Error ≤10%. [d] MeCN/H_2O 1:1 (v/v). [e] MeCN/H_2O 4:1 (v/v).[10]

at 280 nm, and a weaker one at 310 nm. The band centered at 310 nm, which undergoes a first-order decay with the same rate as the decay of the 425 nm band (inset a), is also attributed to the 4-trifluoromethylcumyloxyl radical.

Decay of these two bands is accompanied by a corresponding buildup of optical density at 235 nm attributed to 4-trifluoromethylacetophenone. The decay of the absorption band centered at 280 nm is much slower. This band is assigned to the *tert*-butoxyl radical on the basis of the close analogy with the absorption spectrum of this species, generated independently after 248 nm LFP of an argon-saturated MeCN solution containing 150 mM di-*tert*-butyl peroxide (inset b).[4b]

An interesting observation is that on going from MeCN to MeCN/H_2O 1:1 the absorption band in the visible undergoes a red shift up to 45 nm for all cumyloxyl radicals.[9]

The experimental rate constants for decay of the cumyloxyl radicals, both in MeCN and MeCN/H_2O 1:1, were measured spectrophotometrically by monitoring the decrease in optical density at the visible absorption maximum of the cumyloxyl radicals and (when possible) the corresponding buildup in the UV region due to the formation of the pertinent acetophenone, and they are reported in Table 1, together with the values of λ_{max} for the visible absorption band of the cumyloxyl radicals.

Discussion

Spectral Properties. The data shown in Table 1 confirm that, in agreement with previous reports,[6] the position of the visible absorption band of cumyloxyl radicals is red-shifted by electron-donating ring substituents. A red-shift is also observed on going from MeCN to MeCN/H_2O. This shift was previously reported by some of us for the 4-methoxycumyloxyl radical;[9] we now see that this phenomenon is general and holds for both electron-donating and electron-withdrawing ring substituents.

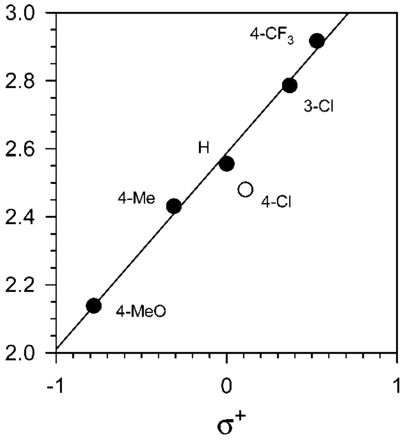


Figure 3. Hammett-type correlation between the experimentally measured energies at the visible absorption maxima and σ^+ substituent constants. $r^2 = 0.994$. Correlation does not include the 4-chlorocumyloxyl radical (○).

Since the visible absorption band results from a $\pi \rightarrow \pi^*$ transition,[6] it is suggested that + R ring substituents promote charge separation in the excited cumyloxyl radical through stabilization of the partial positive charge on the aromatic ring of the incipient radical zwitterion. In agreement with theoretical predictions,[6] the position of the visible absorption band is blue-shifted by the presence of electron-withdrawing ring substituents, 4-chlorocumyloxyl radical representing, however, an exception since for this radical λ_{max} is red-shifted with respect to the unsubstituted cumyloxyl radical by ca. 15 nm. Interestingly, an excellent Hammett-type correlation between the experimentally measured energies at the visible absorption maxima of the cumyloxyl radicals and σ^+ substituent constants is obtained (Figure 3). The 4-chlorocumyloxyl radical is significantly outside the correlation line, a result which is consistent with the importance of the substituents + R effect in determining the position of the visible absorption band.

Going from MeCN to MeCN/H_2O 1:1 results in a red-shift in λ_{max} (between 20 and 45 nm) for all cumyloxyl radicals. Since the position of the visible absorption band of the cumyloxyl radical was found to be solvent independent in a variety of solvents, including dipolar aprotic (MeCN) and protic (AcOH, $(CH_3)_3COH$) ones,[5c,6] the specific effect of water is very remarkable. Probably, this effect is due to the ability of H_2O to solvate both positively and negatively charged species, thus contributing to the stabilization of the excited state, which has a partial radical zwitterionic character.

The absorption band due to the *tert*-butoxyl radical at $\lambda = 280$ nm is only observed after LFP of *tert*-butyl cumyl peroxides bearing electron-withdrawing ring substituents (4-CF_3, 3-Cl, and 4-Cl, respectively) and is in these cases significantly more intense than the cumyloxyl absorption band in the visible. These results indicate that the extinction coefficient for the visible absorption band of 3-chloro, 4-chloro, and 4-trifluoromethylcumyloxyl radicals is smaller than 560 M^{-1} cm^{-1},[11] an observation that

---

(9) Baciocchi, E.; Bietti, M.; Lanzalunga, O.; Steenken, S. *J. Am. Chem. Soc.* **1998**, *120*, 11516−11517.

(10) At higher water concentrations, photoionization, leading to the aromatic radical cation, starts to compete with the homolysis of the peroxidic bond.

(11) The extinction coefficient at the UV absorption band maximum of the *tert*-butoxyl radical (275 nm) has been measured in MeCN as $\epsilon_{275} = 560$ M^{-1} cm^{-1}.[4b]

is in line with the results of theoretical calculations, indicating a decrease in the visible band intensity on going from the 4-methoxy to the 4-trifluoromethylcumyloxyl radical.[6] In contrast, in the case of 4-methyl, 4-methoxy, and 3,4-dimethoxycumyloxyl radicals, the UV absorption is stronger than the *tert*-butoxyl one.[6,11] Moreover, the corresponding acetophenones strongly absorb in the 260−300 nm region (see, for example, Figure 1), and their formation in small amounts shortly after the laser pulse (<100 ns) by β-scission of the corresponding cumyloxyl radicals prevents the observation of the *tert*-butoxyl radical absorption band in the same spectral region.[11]

Reactivity. As already noted, in all cases the rate constants for decay of the cumyloxyl radical are essentially identical (within the experimental error) to the rate constants obtained following the buildup of the product acetophenone. Moreover, it is known that under these conditions hydrogen atom abstraction by the cumyloxyl radicals from the solvent (MeCN or MeCN/H_2O) or from the parent peroxide (used in concentrations between 1.1 and 5.5×10^{-3} M) is negligible.[5c] Therefore, the first-order decay of the visible absorption band can in all cases be assigned to the unimolecular β-scission reaction leading to a methyl radical and the corresponding acetophenone as described in Scheme 1. The value of k_β obtained for the unsubstituted cumyloxyl radical in MeCN ($k_\beta = 7.4 \times 10^5$ s^{-1}, averaging $k\uparrow\_$ and $k\downarrow\_$ from Table 1) is almost identical to that obtained previously by Ingold and Lusztyk in MeCN [$k_\beta = (7.5-7.6) \times 10^5$ s^{-1}], where the radical was generated by 266 or 308 nm light.[5c]

Solvent effects on the rate constants for β-scission of the cumyloxyl radical have been studied in detail;[5b,c,12] the rate of β-scission increases with solvent polarity, an effect that has been attributed to the increased stabilization of the transition state for β-scission through increased solvation of the incipient acetophenone product. Because of the formation of the carbonyl group, the transition state should have a higher dipole moment than the cumyloxyl radical and is therefore more strongly solvated.[13] In line with this hypothesis, we observe that k_β increases on going from MeCN to the more polar MeCN/H_2O 1:1 for all cumyloxyl radicals. For example, for the unsubstituted cumyloxyl radical, k_β increases from 7.4×10^5 s^{-1} in MeCN to 2.7×10^6 s^{-1} in MeCN/H_2O 1:1 (i.e. by a factor 3.6). Interestingly, the same factor is observed on going from MeCN/H_2O 1:1 to H_2O (where a value $k_\beta = 1.0 \times 10^7$ s^{-1} has been determined).[12]

With respect to the substituent effects, the data in Table 1 show that ring substitution does not influence to a significant extent the rate constants for β-scission of the cumyloxyl radicals. Thus, $C_6H_5C(CH_3)_2O^\bullet$ and 4-$MeC_6H_4C(CH_3)_2O^\bullet$ undergo β-scission with very similar k_β values (7.4×10^5 and 7.1×10^5 s^{-1}, respectively), while a slightly higher reactivity is observed for 4-$MeOC_6H_4C(CH_3)_2O^\bullet$, 3,4-$(MeO)_2C_6H_3C(CH_3)_2O^\bullet$, and for the cumyloxyl radicals bearing electron-withdrawing ring substituents ($k_\beta \approx 1.0 \times 10^6$ s^{-1}).

Thus, it appears that no significant charge separation (e.g., as that responsible for the spectral behavior) occurs in the transition state for β-scission of the cumyloxyl radicals. By considering that the ring substituents are expected to influence the stability of the reaction product (substituted acetophenone), the observation of a negligible effect on k_β seems to be in contrast with the proposal of a product-like transition state for β-scission of the cumyloxyl radical, based on the temperature dependence of the secondary α-deuterium isotope effect in methyl radical formation.[14] However, it has been suggested that in alkoxyl radical β-scission to give a carbonyl compound and an alkyl radical, the predominant driving force for cleavage is the stability of the alkyl radical,[4d,15,16] whereas the stability of the carbonyl product plays a minor role.

Experimental Section

Materials. MeCN (Aldrich) of the highest available purity was used as received. Water was obtained from a Millipore-Milli-Q system. Dicumyl peroxide (Aldrich) was recrystallized twice from methanol.

3-Chloro, 4-chloro, 4-trifluoromethyl, 4-methyl, 4-methoxy, 3,4-dimethoxy, and 2,5-dimethoxycumyl alcohols were prepared by reaction of the corresponding arylmagnesium bromide with acetone in anhydrous tetrahydrofuran, purified by column chromatography (silica gel, eluent petroleum ether/ethyl acetate 3:1), and identified by GC−MS and ^{1}H NMR.

tert-Butyl cumyl peroxides were prepared by reaction of the ring-subtituted cumyl alcohols with *tert*-butyl hydroperoxide in the presence of *p*-toluenesulfonic acid, according to a slight modification of a previously described procedure.[17] A 5.0−6.0 M solution of *tert*-butyl hydroperoxide in decane was added to a solution of the cumyl alcohol (*tert*-butyl hydroperoxide/cumyl alcohol ≈ 1.2) in CH_2Cl_2 (purified by filtration through an alumina column) containing *p*-toluenesulfonic acid (alcohol/acid ≈ 10). The reaction mixture was stirred at room temperature and the reaction was followed by TLC. *tert*-Butyl cumyl peroxides were purified by column chromatography (Florisil, eluent pentane) and identified by ^{1}H NMR.[17]

***tert*-Butyl 3-chlorocumyl peroxide:** ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 9H, $C(CH_3)_3$), 1.53 (s, 6H, $ArC(CH_3)_2$), 7.18−7.34 (m, 2H, Ar*H*), 7.42−7.44 (m, 2H, Ar*H*).

***tert*-Butyl 4-trifluoromethylcumyl peroxide:** ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 9H, $C(CH_3)_3$), 1.56 (s, 6H, $ArC(CH_3)_2$), 7.56 (s, 4H, Ar*H*).

***tert*-Butyl 3,4-dimethoxycumyl peroxide:** ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 9H, $C(CH_3)_3$), 1.56 (s, 6H, $ArC(CH_3)_2$), 3.87 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 6.79−7.08 (m, 3H, Ar*H*).

***tert*-Butyl 2,5-dimethoxycumyl peroxide:** ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 9H, $C(CH_3)_3$), 1.59 (s, 6H, $ArC(CH_3)_2$), 3.77 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 6.73−7.31 (m, 3H, Ar*H*).

Time-Resolved LFP Studies. The alkoxyl radicals of interest were generated at room temperature by direct laser flash photolysis (LFP) of symmetric and asymmetric peroxides, using a 248 nm excimer laser (KrF*, Lambda Physik EMG103MSC), providing 20 ns pulses with energies between 5 and 60 mJ/pulse (output power of the laser). Optical detection was employed, with a pulsed xenon lamp as analyzing light. Wavelengths were selected using a monochromator. The time-dependent optical changes were recorded with Tektronix 7612 and 7912 transient recorders, interfaced with a DEC LSI 11/73$^+$ computer, which also controlled the other functions of the instrument and preanalyzed the data.[18] Argon- or oxygen-saturated solutions of the peroxides ($A_{248} \approx 0.3-0.6$) in MeCN or MeCN/H_2O flowed through a 2 mm (in the direction of the

---

(12) Neta, P.; Dizdaroglu, M.; Simic, M. G. *Isr. J. Chem.* **1984**, *24*, 25−28.

(13) We thank a reviewer for this suggestion.

(14) Zavitsas, A. A.; Seltzer, S. *J. Am. Chem. Soc.* **1964**, *86*, 3836−3840.

(15) Kochi, J. K. *J. Am. Chem. Soc.* **1962**, *84*, 1193−1197.

(16) Wilsey, S.; Dowd, P.; Houk, K. N. *J. Org. Chem.* **1999**, *64*, 8801−8811.

(17) Hendrickson, W. H.; Nguyen, C. C.; Nguyen, J. T.; Simons, K. T. *Tetrahedron Lett.* **1995**, *36*, 7217−7220.

(18) Faria, J. L.; Steenken, S. *J. Phys. Chem.* **1993**, *97*, 1924−1930.

laser beam) by 4 mm (in the direction of the analyzing light, 90° geometry) Suprasil quartz cell. All experiments were carried out at about 22 ± 2 °C. Rate constants were obtained by averaging 6−12 values, each consisting of an average of 10−30 laser shots, and were reproducible to within 10%.

Acknowledgment. This work was carried out into the framework of the EU project “Towards Efficient Oxygen Delignification” (Contract No. QLK5-CT-1999-01277).

JO0163041