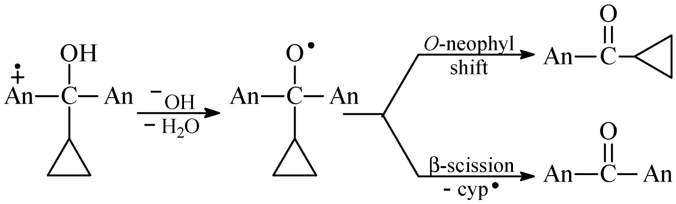
Oxygen Acidity of Ring Methoxylated 1,1-Diarylalkanol Radical Cations Bearing α-Cyclopropyl Groups. The Competition between *O*-Neophyl Shift and C−Cyclopropyl *β*-Scission in the Intermediate 1,1-Diarylalkoxyl Radicals

Massimo Bietti,* Simone Fiorentini, Iria Pèrez Pato, and Michela Salamone

Dipartimento di Scienze e Tecnologie Chimiche, Università "Tor Vergata", Via della Ricerca Scientifica, I-00133 Rome, Italy

bietti@uniroma2.it

Received January 16, 2006



A product and time-resolved kinetic study on the reactivity of the radical cations generated from cyclopropyl(4-methoxyphenyl)phenylmethanol (**1**) and cyclopropyl[bis(4-methoxyphenyl)]methanol (**2**) has been carried out in aqueous solution. In acidic solution, $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ display very low reactivities toward fragmentation, consistent with the presence of groups at C_α (aryl and cyclopropyl) that after $C_\alpha-C_\beta$ bond cleavage would produce relatively unstable carbon-centered radicals. In basic solution, $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ display oxygen acidity, undergoing $^{-}$OH-induced deprotonation from the α-OH group, leading to the corresponding 1,1-diarylalkoxyl radicals $\mathbf{1r}^{\bullet}$ and $\mathbf{2r}^{\bullet}$, respectively, as directly observed by time-resolved spectroscopy. The product distributions observed in the reactions of $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ under these conditions (cyclopropyl phenyl ketone, cyclopropyl(4-methoxyphenyl) ketone, and 4-methoxybenzophenone from $\mathbf{1}^{\bullet+}$; cyclopropyl(4-methoxyphenyl) ketone and 4,4′-dimethoxybenzophenone from $\mathbf{2}^{\bullet+}$) have been rationalized in terms of a water-induced competition between *O*-neophyl shift and C−cyclopropyl *β*-scission in the intermediate 1,1-diarylalkoxyl radicals $\mathbf{1r}^{\bullet}$ and $\mathbf{2r}^{\bullet}$.

Introduction

It has been shown that, in aqueous solution, ring-methoxylated 1-arylalkanol radical cations ($4\text{-MeOC}_6H_4CH(OH)R^{\bullet+}$) exhibit oxygen acidity in addition to the expected and well-known carbon acidity.[1,2] Thus, whereas in acidic solution the radical cations undergo direct $C_\alpha-H$ deprotonation and/or $C_\alpha-R$ bond cleavage (depending on the nature of the R group), at pH ≥ 9, a diffusion-controlled $^{-}$OH-induced reaction ($k_{-OH} \approx 10^{10}$ M $^{-1}s^{-1}$) takes place involving deprotonation at the α-OH group. It was proposed that under the latter conditions the reaction proceeds through the formation of an intermediate arylcarbinyloxyl radical (either directly or via an intermediate radical zwitterion), which then undergoes a formal 1,2-hydrogen-atom shift, converting the oxygen-centered radical into a carbon-centered one (Scheme 1, path **a**) or a $C_\alpha-R$ *β*-fragmentation reaction leading to 4-methoxybenzaldehyde and the radical $R^{\bullet}$ (path **b**).

Very importantly, direct evidence for the formation of an intermediate arylcarbinyloxyl radical was indeed obtained in a pulse radiolysis (PR) study on the reaction of the 4-methoxycumyl alcohol radical cation with $^{-}$OH where, as observed by time-resolved UV−vis spectroscopy, decay of the radical cation was accompanied by the formation of the 4-methoxycumyloxyl radical, precursor of the product 4-methoxyacetophenone (Scheme 2).[3]

It is, however, important to point out that direct evidence for the formation of an intermediate arylcarbinyloxyl radical was obtained only in this case because fragmentation of the

---

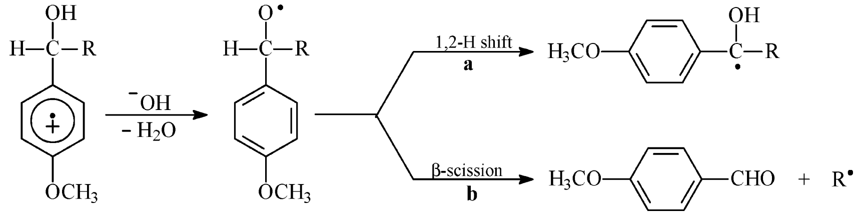
(1) Baciocchi, E.; Bietti, M.; Lanzalunga, O. *Acc. Chem. Res.* **2000**, *33*, 243−251.

(2) Baciocchi, E.; Bietti, M.; Steenken, S. *Chem.*−*Eur. J.* **1999**, *5*, 1785−1793.

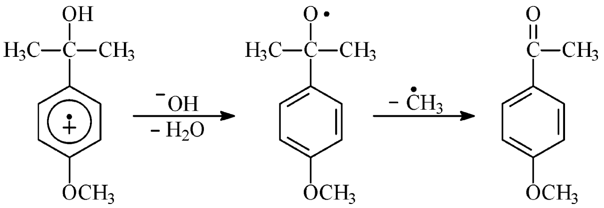
(3) Baciocchi, E.; Bietti, M.; Lanzalunga, O.; Steenken, S. *J. Am. Chem. Soc.* **1998**, *120*, 11516−11517.

10.1021/jo0600860 CCC: \$33.50

SCHEME 1



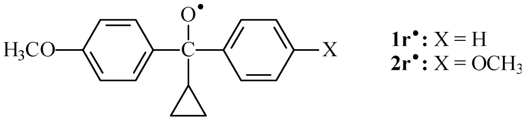
SCHEME 2



4-methoxycumyloxyl radical leads to 4-methoxyacetophenone and ${}^{\bullet}CH_3$, the least stable alkyl radical.[4] With 1-(4-methoxyphenyl)alkanol radical cations bearing α-alkyl groups that can produce, after fragmentation, radical fragments more stable than methyl, no evidence for the formation of an intermediate arylcarbinyloxyl radical was instead obtained,[2] as expected on the basis of the much higher reactivity of these radicals[5,6] as compared to the cumyloxyl one.[4,7,8] Moreover, with the 4-methoxybenzyl alcohol radical cation, no spectroscopic evidence for the formation of an intermediate 4-methoxybenzyloxyl radical was obtained, in line with the reported rate constants for the 1,2-H-atom shift in benzyloxyl radicals ($\approx 10^8$ s^{-1}),[9] which are clearly too high to allow detection of the 4-methoxybenzyloxyl radical under the experimental conditions employed.

Very recently, while investigating the *O*-neophyl rearrangement of ring-substituted 1,1-diarylalkoxyl radicals,[10] we observed that in acetonitrile solution both the cyclopropyl(4-methoxyphenyl)phenylmethoxyl and the cyclopropyl[bis(4-methoxyphenyl)]methoxyl radicals (structures **1r•** and **2r•**, respectively, in Chart 1) underwent a 1,2-aryl shift as the exclusive reaction pathway, with rate constants ($k = 5.1 \times 10^5$ and 2.6×10^5 s^{-1}, respectively) that are lower than that measured previously in acetonitrile for C−methyl β-scission of the 4-methoxycumyloxyl radical ($k = 1.0 \times 10^6$ s^{-1}).[4]

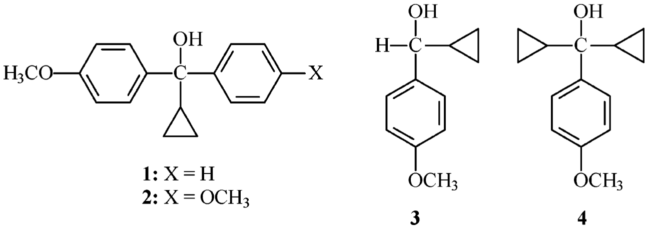
CHART 1



Along this line, we felt that the parent alcohols, namely, cyclopropyl(4-methoxyphenyl)phenylmethanol (**1**) and cyclopropyl[bis(4-methoxyphenyl)]methanol (**2**) could be employed as suitable mechanistic probes to obtain additional evidence on the involvement of alkoxyl radicals in the ⁻OH-induced fragmentation of 1-arylalkanol radical cations.

For this purpose, we have carried out a product and time-resolved kinetic study on the reactivity of the radical cations generated from 1,1-diarylalkanols **1** and **2**. The study has been also extended to 1-(4-methoxyphenyl)alkanols bearing one or two α-cyclopropyl groups (substrates **3** and **4**, respectively, in Chart 2).

CHART 2



Results

Generation of the Radical Cations. The radical cations of substrates **1−4** were generated in aqueous solution by means of chemical radiation (PR) and photochemical techniques (laser flash photolysis (LFP) and steady-state photolysis), employing the sulfate radical anion ($SO_4^{\bullet-}$) as the oxidant. $SO_4^{\bullet-}$ is a strong oxidant that is known to react with ring-methoxylated aromatic compounds via electron transfer to give the corresponding radical cations with $k \geq 5 \times 10^9$ M^{-1}s^{-1} (eq 1: An = 4-MeOC$_6$H$_4$).[2,11,12]

$$\overset{OH}{AnCHR} + SO_4^{\bullet-} \longrightarrow \overset{\overset{\bullet +}{}\;OH}{AnCHR} + SO_4^{2-} \qquad (1)$$

In the PR experiments, $SO_4^{\bullet-}$ was generated by the radiolysis of argon- or oxygen-saturated aqueous solutions containing substrates **1−4** (0.1−1.0 mM), $K_2S_2O_8$ (10 mM), and 2-methyl-2-propanol (0.1−0.5 M), according to eqs 2−4.

$$H_2O \rightsquigarrow H^+, {}^{\bullet}OH, e^-_{aq} \qquad (2)$$

$${}^{\bullet}OH + CH_3C(CH_3)_2OH \rightarrow H_2O + {}^{\bullet}\dot{C}H_2C(CH_3)_2OH \qquad (3)$$

$$e_{aq}^{-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{\bullet-} \qquad (4)$$

Radiolysis of water leads to the formation of the hydroxyl radical (${}^{\bullet}OH$) and the hydrated electron (e_{aq}^-; eq 2). The former

---

[4] Baciocchi, E.; Bietti, M.; Salamone, M.; Steenken, S. *J. Org. Chem.* **2002**, *67*, 2266−2270.

[5] Bietti, M.; Lanzalunga, O.; Salamone, M. *J. Org. Chem.* **2005**, *70*, 1417−1422.

[6] Newcomb, M.; Daublain, P.; Horner, J. H. *J. Org. Chem.* **2002**, *67*, 8669−8671.

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

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

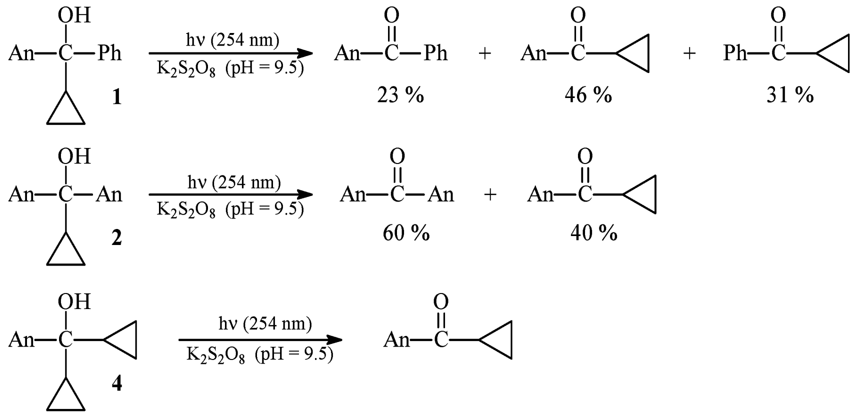
[9] Konya, K. G.; Paul, T.; Lin, S.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **2000**, *122*, 7518−7527.

[10] Aureliano Antunes, C. S.; Bietti, M.; Ercolani, G.; Lanzalunga, O.; Salamone, M. *J. Org. Chem.* **2005**, *70*, 3884−3891.

[11] Neta, P.; Madhavan, V.; Zemel, H.; Fessenden, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 163−164.

[12] O'Neill, P.; Steenken, S.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1975**, *79*, 2773−2779.

SCHEME 3

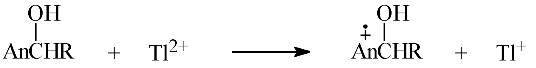


is scavenged by 2-methyl-2-propanol (eq 3; $k = 6 \times 10^8$ $M^{-1}s^{-1}$),[13] while e_{aq}^- reacts with the peroxydisulfate anion, leading to the formation of $SO_4^{\bullet-}$ (eq 4; $k = 1.2 \times 10^{10}$ $M^{-1}s^{-1}$).[13]

In acidic solution, Tl^{2+} was also used as the oxidant, produced by PR of N_2O saturated aqueous solutions. The function of N_2O is to scavenge e_{aq}^-, leading to the formation of an additional hydroxyl radical (eq 5), with $k = 9.1 \times 10^9$ $M^{-1}s^{-1}$.[14] Tl^{2+} is then produced by the oxidation of Tl^+ by $^{\bullet}OH$ (eq 6) with $k = 1.2 \times 10^{10}$ $M^{-1}s^{-1}$.[15] Also, Tl^{2+} reacts with ring methoxylated aromatic substrates by electron transfer to give the corresponding radical cations (eq 7: An = 4-MeOC_6H_4) with $k \approx 5 \times 10^8$ $M^{-1}s^{-1}$.[12]

$$e_{aq}^- + N_2O + H_2O \rightarrow N_2 + {}^{\bullet}OH + {}^{-}OH \qquad (5)$$

$$^{\bullet}OH + Tl^+ + H^+ \rightarrow Tl^{2+} + H_2O \qquad (6)$$



$$\mathrm{An}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{HR} + \mathrm{Tl}^{2+} \longrightarrow \overset{\bullet+}{\mathrm{An}}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{HR} + \mathrm{Tl}^{+}$$

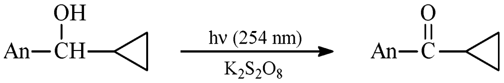
(7)

In the photochemical experiments, $SO_4^{\bullet-}$ was instead generated by UV photolysis of argon- or oxygen-saturated aqueous solutions containing substrates **1**−**4** (0.1−1.0 mM), $K_2S_2O_8$ (0.1 M), and 10% acetonitrile (to improve substrate solubility) or 2-methyl-2-propanol (0.1 M, in the LFP experiments), as described in eq 8.[16,17]

$$S_2O_8^{2-} \xrightarrow{h\nu} 2\ SO_4^{\bullet-} \qquad (8)$$

Product studies. The oxidation of substrates **1**−**4** was carried out at $T = 25$ °C in an argon-saturated aqueous solution (pH = 3.5 or 9.5), employing $SO_4^{\bullet-}$ as the oxidant, generated by steady-state 254-nm photolysis of $S_2O_8^{2-}$, as described in eq 8. With all substrates, the reaction leads to the formation of ring-conjugated ketones (benzophenones and aryl cyclopropyl ketones, see below). To minimize undesired photoreactions of these first-formed products, irradiation times were chosen in such a way as to obtain a limited substrate conversion (≈ 30%). After workup of the reaction mixture, the reaction products were identified by GC (comparison with authentic samples) and GC-MS, and quantitatively determined, together with the unreacted substrate by GC, using bibenzyl as an internal standard.

At pH = 3.5 and 9.5, the reaction of **3** led to the formation of cyclopropyl(4-methoxyphenyl) ketone as the exclusive reaction product, as described in eq 9 (An = 4-MeOC_6H_4).[18]



(9)

At pH = 3.5, photolysis of substrates **1**, **2**, and **4** resulted in an almost complete (≥96%) recovery of the parent compound, accompanied by the formation of negligible amounts (<1%) of the following products: cyclopropyl phenyl ketone, cyclopropyl(4-methoxyphenyl) ketone and 4-methoxybenzophenone from **1**; cyclopropyl(4-methoxyphenyl) ketone and 4,4′-dimethoxybenzophenone from **2**; and cyclopropyl(4-methoxyphenyl) ketone from **4**.

When the reactions of **1**, **2**, and **4** were carried out at pH = 9.5, significantly higher conversions (between 25 and 30%) were instead observed. Under these conditions, the reaction of **1** led to the formation of cyclopropyl phenyl ketone (31%), cyclopropyl(4-methoxyphenyl) ketone (46%), and 4-methoxybenzophenone (23%), as described in Scheme 3 (An = 4-MeOC_6H_4).

Under the same experimental conditions, the reaction of **2** led instead to the formation of 4,4′-dimethoxybenzophenone (60%) and cyclopropyl(4-methoxyphenyl) ketone (40%), while the reaction of **4** led to the exclusive formation of cyclopropyl-(4-methoxyphenyl) ketone (Scheme 3).

Time-Resolved Studies. Spectral Properties. The transients produced after LFP or PR of acidic aqueous solutions (pH ≈ 4) containing substrates **1**−**4** and $K_2S_2O_8$ showed in all cases UV and visible absorption bands centered around 290 and 450 nm, which are analogous to those observed previously for a variety of 1-(4-methoxyphenyl)alkanol radical cations[2,3,19] and, thus, can be reasonably assigned to the corresponding radical cations $\mathbf{1}^{\bullet+}$−$\mathbf{4}^{\bullet+}$, formed by $SO_4^{\bullet-}$-induced one-electron oxidation of the neutral substrates, as described in eq 1.

---

[13] Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513−886.

[14] Janata, E.; Schuler, R. H. *J. Phys. Chem.* **1982**, *86*, 2078−2084.

[15] Schwarz, H. A.; Dodson, R. W. *J. Phys. Chem.* **1984**, *88*, 3643−3647. Asmus, K.-D.; Bonifacic, M.; Toffel, P.; O'Neill, P.; Schulte-Frohlinde, D.; Steenken, S. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1820−1826.

[16] Bietti, M.; Capone, A. *J. Org. Chem.* **2004**, *69*, 482−486.

[17] Steenken, S.; Warren, C. J.; Gilbert, B. C. *J. Chem. Soc., Perkin Trans. 2* **1990**, 335−342.

[18] As a matter of comparison, after a 30 s irradiation, a slightly higher amount of ketone was observed when the reaction was carried out in basic solution (45%, with respect to the starting arylalkanol **3**, at pH = 9.5 as compared to 37% at pH = 3.5).

[19] Bietti, M.; Lanzalunga, O. *J. Org. Chem.* **2002**, *67*, 2632−2638.

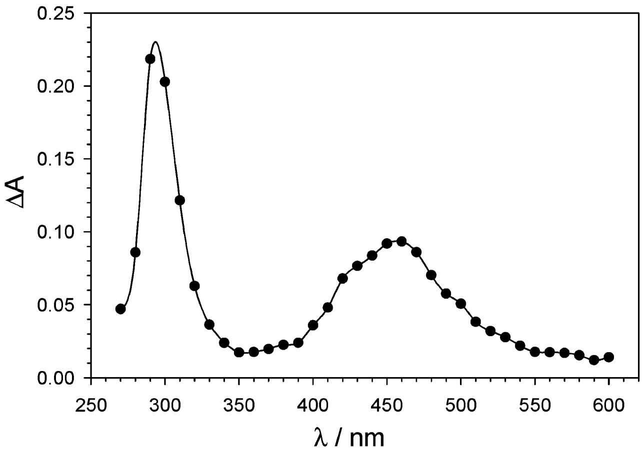


FIGURE 1. Time-resolved absorption spectrum observed after a 266-nm LFP of an argon-saturated aqueous solution (pH = 3.9) containing 0.1 M $K_2S_2O_8$, 0.5 mM **4**, and 0.1 M 2-methyl-2-propanol, recorded 1 μs after the 8-ns, 10-mJ laser pulse.

As an example, Figure 1 shows the time-resolved absorption spectrum observed at 1 μs after 266-nm LFP of an argon-saturated aqueous solution (pH = 3.9) containing **4** (0.5 mM), 2-methyl-2-propanol (0.1 M), and $K_2S_2O_8$ (0.1 M). Visible are two bands centered around 290 and 450 nm that, as mentioned above, are assigned to the radical cation $\mathbf{4}^{\bullet+}$. An identical spectrum was obtained after PR of an argon-saturated aqueous solution (pH = 4.5) containing **4** (0.2 mM), 2-methyl-2-propanol (0.1 M), and $K_2S_2O_8$ (10 mM).

Interestingly, as compared to the 1-(4-methoxyphenyl)alkanol radical cations $\mathbf{3}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$, which display only two bands around 290 and 450 nm, an additional band is present in the time-resolved absorption spectra of 1,1-diarylalkanol radical cations $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$, centered around 700 and 920 nm, respectively.[20] The latter bands are analogous to those described previously for the radical cations of 4-methoxydiphenylmethanol and 4,4′-dimethoxydiphenylmethanol[19] and are thus assigned to an intramolecular charge resonance interaction between the neutral donor and the charged acceptor rings in $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$.

Figure 2 shows the time-resolved absorption spectra observed after PR of an argon-saturated aqueous solution (pH = 9.5) containing **2** (0.4 mM), 2-methyl-2-propanol (0.5 M), and $K_2S_2O_8$ (10 mM). The spectrum recorded after 1.8 μs (empty circles) shows three absorption bands centered around 300, 450, and 920 nm, that are assigned to $\mathbf{2}^{\bullet+}$. The decay of $\mathbf{2}^{\bullet+}$ (insets **a** and **c**) leads to the formation of an intermediate characterized by a broad absorption band at 740 nm (spectrum recorded at 4.8 μs (filled circles) and inset **b**) and whose decay is unaffected by oxygen and is accompanied by a strong buildup in absorption at 300 nm (spectrum recorded at 16 μs (empty squares)), which is only slightly affected by oxygen (inset **d**).

A similar behavior was observed after PR of an argon-saturated aqueous solution (pH = 9.5) containing **1**. The decay of $\mathbf{1}^{\bullet+}$, characterized by three absorption bands centered around 300, 450, and 700 nm, is now accompanied by the formation of an intermediate characterized by a broad absorption band at 660 nm, whose decay leads to a strong buildup in absorption around 300 nm.

Kinetic Studies. In an acidic solution (pH ≤ 4), the decay rates of radical cations $\mathbf{1}^{\bullet+}$–$\mathbf{4}^{\bullet+}$ were measured spectrophotometrically following the change in absorption at the visible absorption band maximum (450 nm). Under these conditions, $\mathbf{3}^{\bullet+}$ was found to decay by a first-order reaction. The decay rates of radical cations $\mathbf{1}^{\bullet+}$, $\mathbf{2}^{\bullet+}$, and $\mathbf{4}^{\bullet+}$ were instead observed to be significantly influenced by the chemical radiation dose or laser intensity and, accordingly, only an upper limit for their decay-rate constant could be determined. These values are displayed in Table 1.

The reactivities of radical cations $\mathbf{1}^{\bullet+}$–$\mathbf{4}^{\bullet+}$ were also studied in an alkaline solution. In the presence of $^{-}$OH, the radical cations decayed with a significantly higher rate as compared to the acidic solution. By plotting the observed rate constants (k_{obs}) against the concentration of $^{-}$OH, a linear dependence was observed (Figure 3), and the second-order rate constants for the reaction of $^{-}$OH with the radical cations (k_{-OH}) were determined. These values are displayed in Table 2.

Discussion

Acidic Solution. The results of product and time-resolved kinetic studies indicate that, in acidic aqueous solution, the decay of $\mathbf{3}^{\bullet+}$ proceeds by the cleavage of the C_α–H bond. Thus, formation of the product cyclopropyl 4-methoxyphenyl ketone can be explained in terms of the oxidation of the α-cyclopropyl-α-hydroxy-4-methoxybenzyl radical formed after the deprotonation of $\mathbf{3}^{\bullet+}$, as shown in Scheme 4, which is in line with the deprotonation reactions of a variety of 1-arylalkanol radical cations described previously.[2,19,21–24]

The exclusive formation of cyclopropyl 4-methoxyphenyl ketone in the one-electron oxidation of **3** clearly indicates that in the intermediate α-cyclopropyl-α-hydroxy-4-methoxybenzyl radical, formed after the deprotonation of $\mathbf{3}^{\bullet+}$, oxidation occurs significantly faster than cyclopropyl ring opening, in agreement with the relatively low rate constants measured for the ring opening of the α-phenyl-substituted cyclopropylcarbinyl radicals.[25]

The deprotonation rate constant measured for $\mathbf{3}^{\bullet+}$ (between 6.2 and 8.4 × 10^3 s^{-1}, depending on the experimental technique employed,[26] see Table 1) is very similar to those determined previously under analogous experimental conditions for the deprotonation of 1-(4-methoxyphenyl)ethanol (**5**) and 1-(4-methoxyphenyl)propan-1-ol (**6**) radical cations ($k = 7.0 \times 10^3$ and 5.4×10^3 s^{-1}, respectively).[2]

It is also interesting to compare the reactivity of $\mathbf{3}^{\bullet+}$ with that observed previously for the structurally related 1-(4-

---

[20] With both **1** and **2**, the time-resolved absorption spectra showed, in addition to the radical cation absorption bands, the immediate formation of a relatively long-lived species in the 380–430-nm region whose decay was unaffected by oxygen. The absorption spectra recorded after PR or LFP of the aqueous solutions containing substrates **1** or **2** and $K_2S_2O_8$ (see, for example, Figure 2) were thus obtained by subtraction of the absorption due to this species recorded in the 380–430-nm region. No additional attempt was made to identify this species.

[21] Lykakis, I. N.; Lestakis, S.; Orfanopoulos, M. *Tetrahedron Lett.* **2003**, *44*, 6247–6251.

[22] Baciocchi, E.; Belvedere, S.; Bietti, M.; Lanzalunga, O. *Eur. J. Org. Chem.* **1998**, *1*, 299–302.

[23] Walling, C.; El-Taliawi, G. M.; Zhao, C. *J. Org. Chem.* **1983**, *48*, 4914–4917.

[24] Trahanovsky, W. S.; Cramer, J. *J. Org. Chem.* **1971**, *36*, 1890–1893.

[25] Halgren, T. A.; Roberts, J. D.; Horner, J. H.; Martinez, F. N.; Tronche, C.; Newcomb, M. *J. Am. Chem. Soc.* **2000**, *122*, 2988–2994.

[26] As the rate constant for deprotonation of $\mathbf{3}^{\bullet+}$ at pH = 3.5 was observed to be influenced by the chemical radiation dose or by the laser intensity (i.e., by the concentration of radicals in solution), the slightly higher value measured when the LFP technique was employed may reflect the fact that relatively lower radical concentrations could be obtained in the PR experiments as compared to the LFP ones.

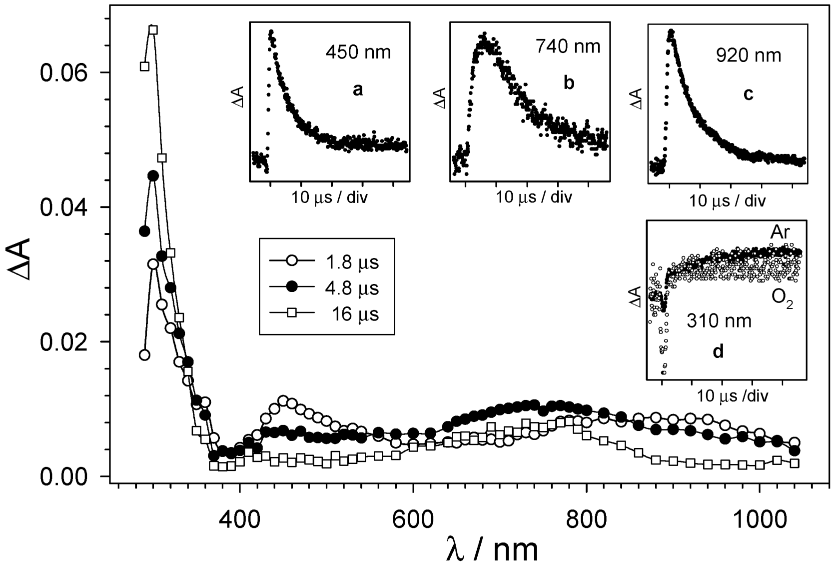


FIGURE 2. Time-resolved absorption spectra observed after PR of an argon-saturated aqueous solution (pH = 9.5) containing **2** (0.4 mM), 2-methyl-2-propanol (0.5 M), and $K_2S_2O_8$ (10 mM), recorded 1.8 (empty circles), 4.8 (filled circles), and 16 μs (empty squares) after the 300-ns, 10-MeV electron pulse. Insets: (a) first-order decay of $\mathbf{2}^{\bullet +}$ monitored at 450 nm; (b) buildup and subsequent decay monitored at 740 nm; (c) first-order decay of $\mathbf{2}^{\bullet +}$ monitored at 920 nm; and (d) buildup monitored at 310 nm under argon (filled circles) and oxygen (empty circles).

TABLE 1. Rate Constants (*k*) for the Decay of Radical Cations $\mathbf{1}^{\bullet +}$−$\mathbf{4}^{\bullet +}$ Generated by PR or LFP in Aqueous Solution (pH ⩽ 4), Measured at *T* = 25 °C

radical cation	conditions[a]	k^b (s^{-1})
$\mathbf{1}^{\bullet +}$	PR, $SO_4^{\bullet -}$	$<10^3$
	LFP, $SO_4^{\bullet -}$	$<5 \times 10^2$
$\mathbf{2}^{\bullet +}$	PR, $SO_4^{\bullet -}$	$<10^3$
	LFP, $SO_4^{\bullet -}$	$<10^3$
$\mathbf{3}^{\bullet +}$	PR, $SO_4^{\bullet -}$	6.4×10^3
	PR, Tl^{2+}	6.2×10^3
	LFP, $SO_4^{\bullet -}$	8.4×10^{3c}
$\mathbf{4}^{\bullet +}$	PR, $SO_4^{\bullet -}$	$<5 \times 10^2$
	LFP, $SO_4^{\bullet -}$	$<5 \times 10^2$

[a] PR, $SO_4^{\bullet -}$: the radical cation was generated by PR (dose ≈ 2 Gy/pulse) as described in eqs 1−4. LFP, $SO_4^{\bullet -}$: the radical cation was generated by LFP (dose < 5 mJ/pulse) as described in eqs 1 and 8. PR, Tl^{2+}: the radical cation was generated by PR (dose ≈ 2 Gy/pulse) as described in eqs 1 and 5−7. [b] Monitored following the decay of absorption at 450 nm. Error < 10%. [c] An identical rate constant was measured in the presence of O_2.

methoxyphenyl)-2-methylpropan-1-ol (**7**) radical cation that undergoes deprotonation in competition with C_α−C_β bond cleavage (product ratio C_α−H/C_α−C_β ≈ 9) with an *overall* rate constant $k = 3.5 \times 10^3$ s^{-1}.[2] The absence of products derived from the C_α−C_β bond cleavage pathway in $\mathbf{3}^{\bullet +}$ can be reasonably explained in terms of the significantly lower stability of the cyclopropyl radical, as compared to the 2-propyl one.[27,28] The decrease in the deprotonation rate constant observed on going from $\mathbf{5}^{\bullet +}$ to $\mathbf{7}^{\bullet +}$ has been explained in terms of the operation of a stereoelectronic effect: the bulkier the α-alkyl group, the more energetically costly it is to reach the conformation most suitable for deprotonation, that is, the one where the C_α−H bond is collinear with the π system, as a result of the increasingly unfavorable interaction of the alkyl group with the *ortho*-hydrogen atoms.[2] In this respect, the observation that the deprotonation rate constant for $\mathbf{3}^{\bullet +}$ is higher than that determined for $\mathbf{7}^{\bullet +}$ may indicate that as a result of the geometrical constraints associated with the cyclopropyl group, the conformation most suitable for deprotonation can be reached more efficiently in $\mathbf{3}^{\bullet +}$ than in $\mathbf{7}^{\bullet +}$.

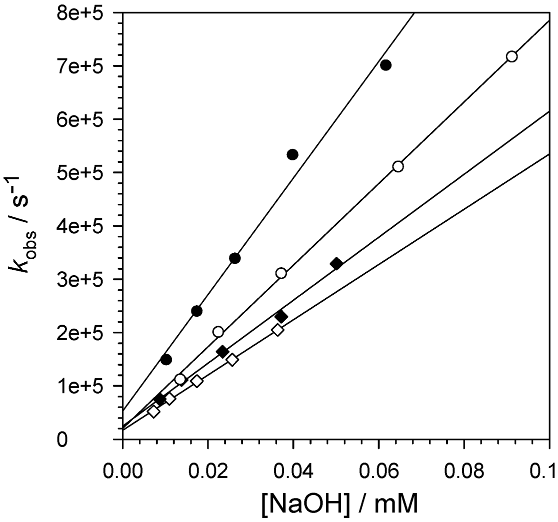


FIGURE 3. Plots of k_{obs} against the concentration of NaOH for the reactions of the radical cations $\mathbf{1}^{\bullet +}$−$\mathbf{4}^{\bullet +}$. $\mathbf{1}^{\bullet +}$ (filled squares): slope = 5.9×10^9 M^{-1} s^{-1}, $r^2 = 0.9928$. $\mathbf{2}^{\bullet +}$ (empty squares): slope = 5.2×10^9 M^{-1} s^{-1}, $r^2 = 0.9989$. $\mathbf{3}^{\bullet +}$ (filled circles): slope = 1.1×10^{10} M^{-1} s^{-1}, $r^2 = 0.9853$. $\mathbf{4}^{\bullet +}$ (empty circles): slope = 7.7×10^9 M^{-1} s^{-1}, $r^2 = 0.9989$.

With substrates **1**, **2**, and **4**, product studies carried out at pH = 3.5 showed an almost complete substrate recovery, accompanied by the formation of negligible amounts of oxidation products. A similar behavior was observed previously for the one-electron oxidation of 4-methoxycumyl alcohol in an acidic aqueous solution.[3] Clearly, with tertiary 1-arylalkanol radical cations C_α−H, deprotonation is not possible, and the presence

---

(27) Based on the $(CH_3)_2CH$−H and c-C_3H_5−H BDEs: 96.3 and 106.3 kcal mol^{-1}, respectively (see ref 28).

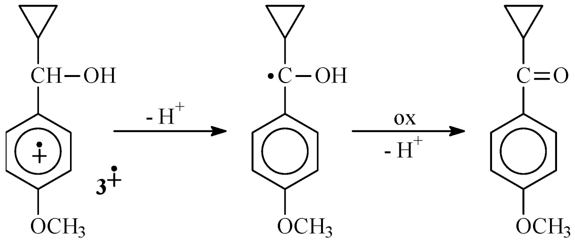
(28) Luo, Y.-R. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRC Press: Boca Raton, FL, 2003.

TABLE 2. Second-Order Rate Constants ($k_{-\mathrm{OH}}$) for the $^{-}$OH−Induced Decay of Radical Cations $\mathbf{1}^{\bullet+}$−$\mathbf{4}^{\bullet+a}$

radical cation	$k_{-\mathrm{OH}}{}^{b}$ ($\mathrm{M^{-1}\ s^{-1}}$)
$\mathbf{1}^{\bullet+}$	5.9×10^{9}
$\mathbf{2}^{\bullet+}$	5.2×10^{9}
$\mathbf{3}^{\bullet+}$	1.1×10^{10c}
$\mathbf{4}^{\bullet+}$	6.0×10^{9}
	7.7×10^{9c}

[a] The radical cations were generated by PR (dose ≈ 5 Gy/pulse) of argon-saturated aqueous solutions (T = 25 °C) containing the substrate (0.4−1.0 mM), $K_2S_2O_8$ (10 mM), 2-methyl-2-propanol (0.5 M), and $Na_2B_4O_7 \times 10\ H_2O$ (1 mM). [b] The observed rate constants (k_{obs}) were measured by monitoring the decay of absorption at 450 nm. The second-order rate constants for the reaction of the radical cations with $^{-}$OH ($k_{-\mathrm{OH}}$) were obtained from the slope of the k_{obs} versus [NaOH] plots. Error < 10%. [c] In the presence of 0.1 M 2-methyl-2-propanol.

SCHEME 4



of groups at C_α that after C_α−C_β bond cleavage would produce relatively unstable radicals (cyclopropyl and 4-methoxyphenyl)[28] strongly depresses their side-chain fragmentation reactivity. This behavior is also reflected by the results of time-resolved kinetic studies where the decay rates of $\mathbf{1}^{\bullet+}$, $\mathbf{2}^{\bullet+}$, and $\mathbf{4}^{\bullet+}$ were observed to be strongly dose-dependent, and, due to instrumental limits, only an upper limit for their decay rate constants could be determined.[29]

Basic Solution. When the decays of radical cations $\mathbf{1}^{\bullet+}$−$\mathbf{4}^{\bullet+}$ are studied in the presence of $^{-}$OH, a completely different situation holds. The $^{-}$OH-induced decay of the radical cations occurs with rate constants ($k_{-\mathrm{OH}}$ between 5.2×10^{9} and $1.1 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$, see Table 2) that approach the diffusion limit. These values are indicative of α-OH deprotonation, as previously discussed for 1-(4-methoxyphenyl)alkanol radical cations,[1−3,19] indicating that under these conditions, $\mathbf{1}^{\bullet+}$−$\mathbf{4}^{\bullet+}$ exhibit *oxygen acidity*.

Very importantly, the time-resolved absorption spectra presented in Figure 2, observed after PR of an argon-saturated aqueous solution (pH = 9.5) containing **2**, clearly show that the decay of $\mathbf{2}^{\bullet+}$ at 450 and 920 nm (see also insets **a** and **c**) leads to the formation of an intermediate (two isosbestic points are visible at 550 and 850 nm) characterized by a broad absorption band centered at 740 nm that subsequently decays (inset **b**), giving rise to a strong buildup in absorption at 300 nm (inset **d**). In full agreement with the results obtained previously for the $^{-}$OH-induced α-OH deprotonation of the 4-methoxycumyl alcohol radical cation in alkaline aqueous solution (see Scheme 2),[3] the 740-nm absorption band can be assigned to the cyclopropyl[bis(4-methoxyphenyl)]methoxyl radical ($\mathbf{2r}^{\bullet}$), formed by the α-OH deprotonation from $\mathbf{2}^{\bullet+}$ (Scheme 5, X = OCH_3), for which a $\lambda_{\max}$ of 640 nm was previously reported in acetonitrile.[10]

An analogous behavior has been observed for $\mathbf{1}^{\bullet+}$ under the same experimental conditions: the decay of $\mathbf{1}^{\bullet+}$ at 450 and 700 nm leads to the formation of an intermediate characterized by a broad absorption band centered at 660 nm, which is assigned to the cyclopropyl(4-methoxyphenyl)phenylmethoxyl radical ($\mathbf{1r}^{\bullet}$), formed by α-OH deprotonation from $\mathbf{1}^{\bullet+}$ (Scheme 5, X = H), for which a $\lambda_{\max}$ of 610 nm was previously reported in acetonitrile.[10]

The observation of a significant red-shift in the position of the visible absorption band maximum of arylcarbinyloxyl radicals on going from acetonitrile to water is well-documented.[3,4,30] This effect has been observed only with protic solvents characterized by very high values of the normalized empirical solvent polarity parameter $E_T{}^N$, such as water and trifluoroethanol.[31,32] As it has been pointed out that the $E_T{}^N$ parameter is mainly related to the solvent anion solvating ability,[33] the observation of this effect is in line with the previous indication that the arylcarbinyloxyl radical visible absorption band results from a $\pi \rightarrow \pi^*$ transition, which determines an increase of electron density on the oxygen atom on going from the ground to the excited state.[34,35]

The intermediacy of 1,1-diarylalkoxyl radicals $\mathbf{1r}^{\bullet}$ and $\mathbf{2r}^{\bullet}$ in the reactions of $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ in alkaline aqueous solution is also supported by the results of product studies carried out at pH = 9.5 after the photolysis of **1** and **2** in the presence of $K_2S_2O_8$. As mentioned above (see Scheme 3), the reaction of **1** leads to the formation of cyclopropyl phenyl ketone (31%), cyclopropyl(4-methoxyphenyl) ketone (46%), and 4-methoxybenzophenone (23%), while the reaction of **2** leads to the formation of 4,4′-dimethoxybenzophenone (60%) and cyclopropyl(4-methoxyphenyl) ketone (40%). The formation of arylcyclopropyl ketones in the reactions of **1** and **2** can be explained in terms of an *O*-neophyl rearrangement in the corresponding radicals $\mathbf{1r}^{\bullet}$ and $\mathbf{2r}^{\bullet}$, formed after α-OH deprotonation from $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$, respectively. In this context, we have recently observed that the *O*-neophyl shift in $\mathbf{1r}^{\bullet}$ and $\mathbf{2r}^{\bullet}$, generated by the photolysis of CH_2Cl_2 solutions containing the parent 1,1-diarylalkanol (**1** or **2**, respectively), (diacetoxy)iodobenzene (DIB), and I_2, that is, under bona fide conditions for alkoxyl radical generation,[36] leads to the formation of the pertinent arylcyclopropyl ketones,[10] as described in Scheme 6 (An = 4-MeOC_6H_4) for the reaction of **1**.

Quite importantly, the molar ratio (Q) of ring-substituted and unsubstituted aryl cyclopropyl ketones obtained in alkaline aqueous solution for **1** after photolysis in the presence of $S_2O_8{}^{2-}$ (Q = 1.48) is very similar to that obtained previously in CH_2Cl_2 employing DIB/I_2 (Q = 1.64).[10] This result strongly supports the formation of a common intermediate, that is, radical $\mathbf{1r}^{\bullet}$, with the two systems. The results obtained in the present study confirm that migration of the unsubstituted phenyl ring is favored over that of the methoxylated one,[10] and indicate

---

[29] As a matter of comparison, in acidic aqueous solution, the 1-(4-methoxyphenyl)-2,2-dimethylpropan-1-ol radical cation undergoes C_α−C_β bond cleavage to give the relatively stable *tert*-butyl radical with $k = 1.5 \times 10^{5}\ \mathrm{s^{-1}}$ (see ref 2).

[30] Bietti, M.; Gente, G.; Salamone, M. *J. Org. Chem.* **2005**, *70*, 6820−6826.

[31] MeCN, CF_3CH_2OH, and H_2O are characterized by the following $E_T{}^N$ values: 0.460, 0.898, and 1.000, respectively (see ref 32).

[32] Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; Wiley-VCH: Weinheim, Germany, 2003.

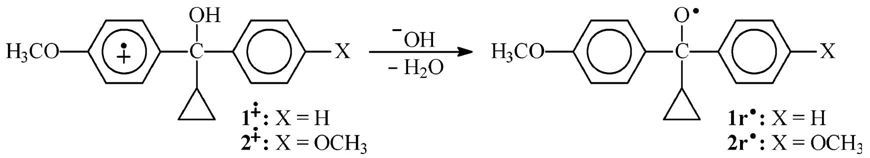
[33] See ref 32, pp 462−463.

[34] 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.

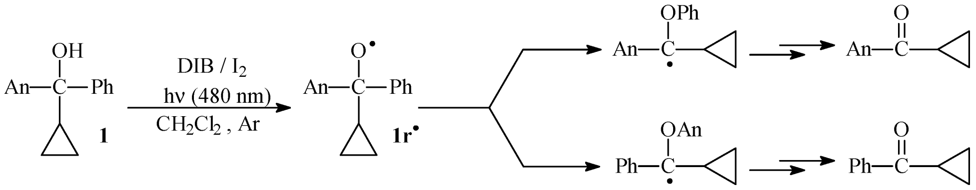
[35] Avila, D. V.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 6576−6577.

[36] See, for example: Suárez, E.; Rodriguez, M. S. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: Weinheim, Germany, 2001; Vol. 2, pp 440−454 and references therein.

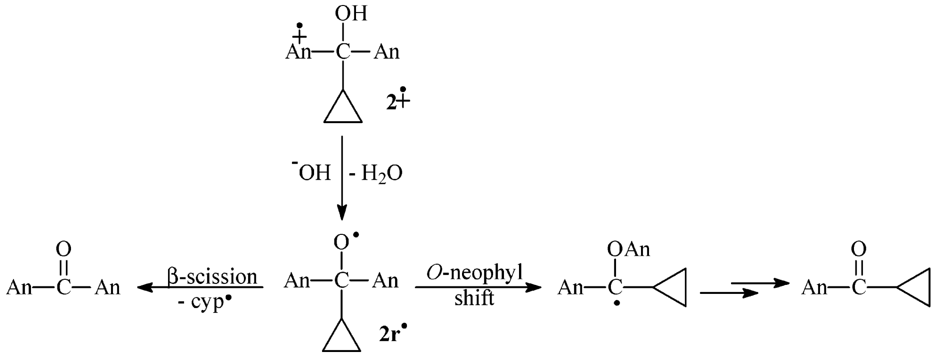
SCHEME 5



SCHEME 6



SCHEME 7



moreover that the solvent does not influence to any significant extent the relative importance of the two competing rearrangement pathways of **1r**$^\bullet$.

However, as mentioned above, when the reactions of radicals **1r**$^\bullet$ and **2r**$^\bullet$ were studied in CH_2Cl_2, the exclusive formation of products derived from an *O*-neophyl shift (arylcyclopropyl ketones) was observed.[10] In alkaline aqueous solution, in addition to these products, substantial amounts of ring-methoxylated benzophenones (23 and 60% from **1** and **2**, respectively) were also observed. The formation of the latter products can be reasonably explained in terms of a C−cyclopropyl β-scission reaction in both **1r**$^\bullet$ and **2r**$^\bullet$.[37] Accordingly, it is well-known that the rate constant for the β-scission of alkoxyl radicals is significantly accelerated by increasing solvent polarity,[4,6,8,30,38] while, on the other hand, we have recently shown that the rate constant for the *O*-neophyl shift of 1,1-diarylalkoxyl radicals decreases by increasing solvent polarity.[40] Along this line, the product distributions observed in the reactions of $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ in alkaline aqueous solution can be rationalized in terms of the competition between *O*-neophyl shift and C−cyclopropyl β-scission in the intermediate 1,1-diarylalkoxyl radicals **1r**$^\bullet$ and **2r**$^\bullet$, as described in Scheme 7 (An = 4-MeOC$_6$H$_4$) for $\mathbf{2}^{\bullet+}$.[41]

The observation that the importance of the β-scission pathway increases on going from $\mathbf{1}^{\bullet+}$ to $\mathbf{2}^{\bullet+}$ is also in agreement with this picture, as the rate constant for C−cyclopropyl β-scission is not expected to be influenced by the presence of ring substituents,[4] whereas the rate constant for the 1,2-aryl shift was observed to decrease on going from radical **1r**$^\bullet$ to **2r**$^\bullet$ ($k = 5.1 \times 10^5$ and $2.6 \times 10^5\ s^{-1}$, respectively, in MeCN).[10]

With $\mathbf{3}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$, no spectroscopic evidence for the formation of an intermediate alkoxyl radical was instead obtained, even though, as mentioned above, the k_{-OH} values displayed in Table 2 are in line with reactions that proceed through $^-$OH-induced α-OH deprotonation in the radical cations.

At pH = 9.5, the reactions of both **3** and **4** led to the exclusive formation of cyclopropyl(4-methoxyphenyl) ketone. In the reaction of **3**, the formation of this product can be explained according to Scheme 8, in line with the mechanism proposed previously for 1-(4-methoxyphenyl)alkanol radical cations (see Scheme 1, path **a**).[2,19]

The radical cation $\mathbf{3}^{\bullet+}$ undergoes α-OH deprotonation to give an intermediate alkoxyl radical (**3r**$^\bullet$) that is converted into an α-cyclopropyl-α-hydroxy-4-methoxybenzyl radical via a 1,2-H-atom shift. This radical is then deprotonated to give the corresponding radical anion,[9,19] which is finally oxidized in the reaction medium to cyclopropyl(4-methoxyphenyl) ketone. As

---

[37] For a critical discussion on C−cyclopropyl β-scission reactions in arylcarbinyloxyl radicals, see ref 30.

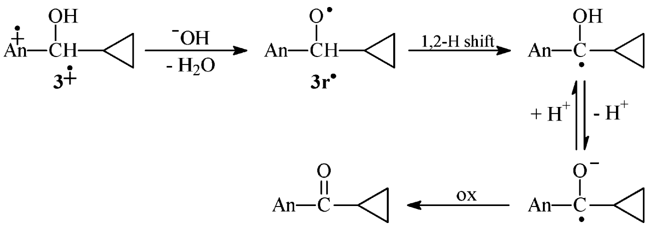
[38] As an example, the rate constant for β-scission of the cumyloxyl radical increases from $3.7 \times 10^5\ s^{-1}$ in benzene (see ref 8) to $1.0 \times 10^7\ s^{-1}$ in H_2O (see ref 39).

[39] Neta, P.; Dizdaroglu, M.; Simic, M. G. *Isr. J. Chem.* **1984**, *24*, 25−28.

[40] Bietti, M.; Salamone, M. *J. Org. Chem.* **2005**, *70*, 10603−10606.

[41] According to this picture, the strong buildup in absorption observed at 300 nm after the $^-$OH-induced decay of $\mathbf{2}^{\bullet+}$ (Figure 2, inset **d**) can be reasonably assigned to the superimposition of the absorption bands due to 4, 4′-dimethoxybenzophenone, for which $\lambda_{max} = 295$ nm in aqueous solution (see ref 19) and the α-cyclopropyl-α-4-methoxyphenoxy-4-methoxybenzyl radical, for which $\lambda_{max} = 295$ nm in MeCN (as observed when generated after a 1,2-aryl shift in the precursor, cyclopropyl[bis(4-methoxyphenyl)]-methoxyl radical), deriving from the C−cyclopropyl β-scission and *O*-neophyl shift, respectively, in the intermediate cyclopropyl[bis(4-methoxyphenyl)]methoxyl radical **2r**$^\bullet$. The observation that this absorption is only slightly affected by oxygen is in line with this assignment, as only the decay of the rearranged carbon-centered radical, formed in smaller amounts as compared to 4, 4′-dimethoxybenzophenone, is affected by oxygen.

SCHEME 8



mentioned above, a rate constant around 10^8 s^{-1} can be reasonably expected for the 1,2-H-atom shift in **3r**$^\bullet$,[9] and, thus, this intermediate escapes detection under the experimental conditions employed in the present study.

In the reaction of **4**, the formation of cyclopropyl(4-methoxyphenyl) ketone can be explained as described previously for the 4-methoxycumyl alcohol radical cation (see Scheme 2)[3] in terms of the $^{-}$OH-induced α-OH deprotonation of **4**$^{\bullet+}$ to give an alkoxyl radical (**4r**$^\bullet$) which then undergoes C−cyclopropyl β-scission, leading to the ketone. Because a rate constant $>10^7$ s^{-1} can be reasonably expected for the β-scission of **4r**$^\bullet$ in aqueous solution,[42] in this case also, it was not possible to detect this intermediate under the experimental conditions employed.

In conclusion, by means of time-resolved studies carried out in alkaline aqueous solution, direct spectroscopic evidence for the formation of 1,1-diarylalkoxyl radicals **1r**$^\bullet$ and **2r**$^\bullet$, following $^{-}$OH-induced α-OH deprotonation of the radical cations generated from cyclopropyl(4-methoxyphenyl)phenylmethanol (**1**) and cyclopropyl[bis(4-methoxyphenyl)]methanol (**2**), has been obtained, in agreement with the results obtained previously for the 4-methoxycumyl alcohol radical cation. This mechanistic picture is also well-supported by the results of product studies carried out after the one-electron oxidations of **1** and **2** at pH = 9.5. In particular, as opposite kinetic solvent effects have been observed for the *O*-neophyl shift and the C−C β-scission in arylcarbinyloxyl radicals, the product distributions observed in the reactions of **1** and **2** under these conditions are in line with a water-induced competition between the *O*-neophyl shift and the C−cyclopropyl β-scission in the intermediate 1,1-diarylalkoxyl radicals **1r**$^\bullet$ and **2r**$^\bullet$.

Experimental Section

Reagents. Potassium peroxydisulfate, sodium hydroxide, disodium tetraborate decahydrate, perchloric acid, acetonitrile, and 2-methyl-2-propanol were of the highest commercial quality available. Milli-Q-filtered (Millipore) water was used for all solutions.

A commercial sample of cyclopropyl(4-methoxyphenyl)phenylmethanol (**1**) was used as received. Cyclopropyl[bis(4-methoxyphenyl)]methanol (**2**) was available from a previous study.[10] α-Cyclopropyl(4-methoxyphenyl)methanol (**3**) was prepared by the reaction of 4-methoxybenzaldehyde with cyclopropylmagnesium chloride in anhydrous tetrahydrofuran,[43] purified by column chromatography (silica gel; eluent, hexane/ethyl acetate, 5:1), and identified by ^{1}H NMR and GC-MS. ^{1}H NMR (CDCl$_3$): δ 7.36−7.33 (m, 2H), 6.90−6.87 (m, 2H), 3.96 (d, 1H, J = 8 Hz), 3.80 (s, 3H), 1.26−1.14 (m, 1H), 0.64−0.47 (m, 3H), 0.46−0.31 (m, 1H). GC-MS (*m*/*z*, relative abundance): 178 (M$^+$), 150 (100), 135, 121, 109, 91, 77, 51.

α,α-Dicyclopropyl(4-methoxyphenyl)methanol (**4**) was prepared by the reaction of cyclopropyl(4-methoxyphenyl) ketone with cyclopropylmagnesium chloride in anhydrous tetrahydrofuran, purified by column chromatography (silica gel; eluent, hexane/ethyl acetate, 5:1), and identified by ^{1}H NMR and GC-MS. ^{1}H NMR (CDCl$_3$):[44] δ 7.51−7.48 (m, 2H), 6.88−6.85 (m, 2H), 3.81 (s, 3H), 1.43 (s, 1H), 1.23−1.13 (m, 2H), 0.57−0.48 (m, 4H), 0.41−0.34 (m, 4H). GC-MS (*m*/*z*, relative abundance): 218 (M$^+$), 190, 177, 173, 159, 135 (100), 121, 115, 91,77,69,55.

The purity of the synthesized compounds **3** and **4** was in both cases >99%.

Product Studies. In a typical experiment, 10 mL of an argon-saturated aqueous solution (pH = 3.5 or 9.5) containing 10% MeCN (to improve the solubility of substrates **1** and **2**), the substrate (**1**−**4**, 1 mM), and $K_2S_2O_8$ (0.1 M) were irradiated for 30 s, employing a photochemical reactor equipped with 4 × 15 W lamps with the emission at 254 nm. The reactor was a cylindrical flask equipped with a water cooling jacket thermostated at T = 25 °C. To minimize undesired photoreactions of the first-formed ring-conjugated carbonyl products, the irradiation times were chosen in such a way as to obtain a limited substrate conversion (≈30%). In acidic solution, the pH was adjusted to 3.5 with $HClO_4$. In basic solution, 10 mM $Na_2B_4O_7 \times 10\ H_2O$ was added, and the pH was adjusted to 9.5 with NaOH. After irradiation, the reaction mixture was extracted with Et_2O (3 × 10 mL), and the combined organic layers were dried over anhydrous sodium sulfate. Reaction products were identified by GC (comparison with authentic samples) and GC-MS and quantitatively determined by GC using bibenzyl as an internal standard. Good mass balances (>90%) were obtained in all experiments. At least three independent product studies were carried out for every substrate under identical experimental conditions. Blank experiments performed in the absence of irradiation, or by irradiating in the absence of $K_2S_2O_8$, resulted in an almost complete (≥98%) substrate recovery accompanied by the formation of negligible amounts (<1%) of reaction products.

Time-Resolved Studies. The PR experiments were performed using a 10 MeV electron linear accelerator that supplied 300-ns to 1-μs pulses, with doses such that 1−10 μM radicals were produced. Experiments were performed at room temperature using argon-saturated aqueous solutions containing the substrate (0.1−1.0 mM), potassium peroxydisulfate (10 mM), and 2-methyl-2-propanol (0.1−0.5 M). The pH of the solutions was adjusted with $HClO_4$ or NaOH. A flow system was employed in all the experiments. The rate constants (k_{dec}) were obtained by averaging 4 to 8 values, each consisting of the average of 3 to 10 shots and were reproducible to within 10%.

The second-order rate constants for the reaction of the radical cations with $^{-}$OH ($k_{-\mathrm{OH}}$) were obtained from the slopes of the plots of the observed rates (k_{obs}) versus the concentration of NaOH. For these experiments, argon-saturated solutions containing 0.4−1.0 mM substrate, 10 mM potassium peroxydisulfate, 0.1−0.5 M 2-methyl-2-propanol, and 1 mM $Na_2B_4O_7 \times 10\ H_2O$ were employed.

LFP experiments were carried out with a laser kinetic spectrometer that supplied 8-ns pulses, using the fourth harmonic (266 nm) of a Q-switched Nd:YAG laser. The laser energy was adjusted to ≤10 mJ/pulse by the use of the appropriate filter. A 3-mL Suprasil quartz cell (10 mm × 10 mm) was used for all experiments. Argon- or oxygen-saturated aqueous solutions (pH = 3.5) containing the substrate, **1**−**4** (0.1−0.5 mM), $K_2S_2O_8$ (0.1 M), and 2-methyl-2-

---

[42] By comparing the rate constants for C−methyl β-scission for the cumyloxyl radical measured in acetonitrile, trifluoroethanol, and water (k = 7.1×10^5, 6.1×10^6, and 1.0×10^7 s^{-1}, respectively (see refs 30 and 39)) with those for C−cyclopropyl β-scission in the α,α-dicyclopropylphenylmethoxyl one measured in acetonitrile and trifluoroethanol (k = 1.3×10^6 and 1.6×10^7 s^{-1}, respectively (see ref 30)), a rate constant greater than 1.6×10^7 s^{-1} can be reasonably expected for β-scission of the α,α-dicyclopropyl(4-methoxyphenyl)methoxyl radical **4r**$^\bullet$ in water.

[43] McCormick, J. P.; Fitterman, A. S.; Barton, D. L. *J. Org. Chem.* **1981**, *46*, 4708−4712.

[44] Olah, G. A.; Surya Prakash, G. K.; Liang, G. *J. Org. Chem.* **1977**, *42*, 2666−2671.

propanol (0.1 M) were used. All the experiments were carried out at $T = 25 \pm 0.5$ °C under magnetic stirring.

Acknowledgment. Financial support from the Ministero dell'Istruzione dell'Università e della Ricerca (MIUR) is gratefully acknowledged. PR experiments were performed at the Free Radical Research Facility, Daresbury Laboratory, Warrington, U.K. under the support of the European Commission's Transnational Access to Major Research Infrastructures. We thank Prof. Basilio Pispisa and Dr. Lorenzo Stella for the use and assistance in the use of the LFP equipment and Mr. Luigi Gastaldo (Helios Italquartz (www.heliositalquartz.com)) for providing us with a photochemical reactor.

JO0600860