Spectral Properties and Reactivity of Diarylmethanol Radical Cations in Aqueous Solution. Evidence for Intramolecular Charge Resonance[1]

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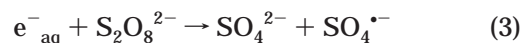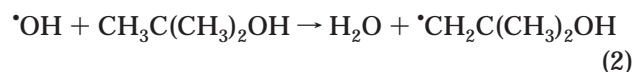
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Spectral properties and reactivities of ring-methoxylated diarylmethane and diarylmethanol radical cations, generated in aqueous solution by pulse and γ-radiolysis and by the one-electron chemical oxidant potassium 12-tungstocobalt(III)ate, have been studied. The radical cations display three bands in the UV, visible, and vis–NIR regions of the spectrum. The vis–NIR band is assigned to an intramolecular charge resonance interaction (CR) between the neutral donor and charged acceptor rings, as indicated by the observation that the relative intensity of the vis–NIR band compared to that of the UV and visible bands does not increase with increasing substrate concentration and that the position and intensity of this band is influenced by the ring-substitution pattern. In acidic solution (pH = 4), monomethoxylated diarylmethanol radical cations **1a[•+]**–**1e[•+]** decay by C_α-H deprotonation [$k = (1.7-1.9) \times 10^4$ s^{-1}] through the intermediacy of a ketyl radical, which is further oxidized in the reaction medium to give the corresponding benzophenones, as evidenced by both time-resolved spectroscopic and product studies. With the dimethoxylated radical cation **2[•+]**, C_α-H deprotonation is instead significantly slower ($k = 6.7 \times 10^2$ s^{-1}). In basic solution, **1a[•+]**–**1e[•+]** undergo $^-$OH-induced deprotonation from the α-OH group with $k_{OH^-} \approx 1.4 \times 10^{10}$ M^{-1} s^{-1}, leading to a ketyl radical anion, which is oxidized in the reaction medium to the corresponding benzophenone.

Side-chain deprotonation of alkylaromatic radical cations represents one of the main reaction pathways of these important reactive intermediates, and the reactions of this class of carbon acids attract continuous attention.[3] In relation to our interest on this topic, we have recently shown the existence of a pH-dependent mechanistic change for the deprotonation reactions of 1-(4-methoxyphenyl)alkanol radical cations in aqueous solution. Accordingly, while in neutral and acidic solution 4-methoxybenzyl alcohol radical cation undergoes C_α-H deprotonation to give the corresponding benzylic radical, in alkaline solution it reacts with $^-$OH at a diffusion-controlled rate undergoing O–H deprotonation.[4,5] To obtain a better understanding of this mechanistic picture, we felt that useful information could be provided through the study of the reactivity of mono- and dimethoxylated diarylmethanol radical cations (compounds **1a**–**1e** and

2 in Chart 1), i.e., substrates containing an additional aromatic ring on the benzylic carbon, both in acidic and basic solution. For comparison, the radical cations of diarylmethanes **3a** and **3c** have also been investigated. The results of these studies are reported herein.

Results

Generation of the Radical Cations. Radical cations of substrates **1**–**3** were generated in aqueous solution by means of radiation chemical techniques (pulse radiolysis and steady-state ^{60}Co γ-radiolysis) employing sulfate radical anion (SO$_4^{•-}$) as the oxidant (method 1: eqs 1–4, X = H, OH):

$$H_2O \xrightarrow{h\nu,\ \gamma\text{-ray}} H^+,\ ^\bullet OH,\ e^-_{aq} \qquad (1)$$

$$^\bullet OH + CH_3C(CH_3)_2OH \rightarrow H_2O + {}^\bullet CH_2C(CH_3)_2OH \qquad (2)$$

$$e^-_{aq} + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{•-} \qquad (3)$$

$$SO_4^{•-} + ArCH(X)Ar' \rightarrow SO_4^{2-} + Ar^{•+}CH(X)Ar' \quad (4)$$

The hydroxyl radical ($^\bullet$OH) is scavenged by 2-methyl-2-propanol (eq 2) with $k = 6 \times 10^8$ M^{-1} s^{-1},[6] while the

(1) This paper is dedicated to Professor Enrico Baciocchi on the occasion of his 70th birthday.
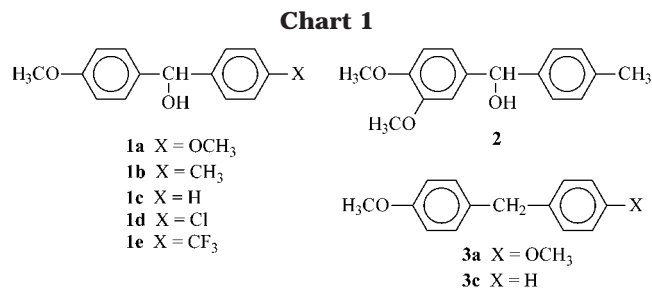
(2) (a) Universitá Tor Vergata. (b) Universitá La Sapienza. E-mail: lanzalunga@uniroma1.it.

(3) See, for example: (a) *Electron Transfer in Chemistry (Organic, Organometallic, and Inorganic Molecules; Part 1: Organic Molecules)*; Balzani, V., Ed., Wiley-VCH: Weinheim, 2001; Vol. 2. (b) Baciocchi, E.; Lanzalunga, O. *Acc. Chem. Res.* **2000,** *33,* 243–251. (c) Parker, V. D.; Zhao, Y.; Lu, Y.; Zheng, G. *J. Am. Chem. Soc.* **1998,** *120,* 12720–12727. (d) Bockman, T. M.; Hubig, S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1998,** *120,* 2826–2830. (e) Freccero, M.; Pratt, A.; Albini, A.; Long, C. *J. Am. Chem. Soc.* **1998,** *120,* 284–297.

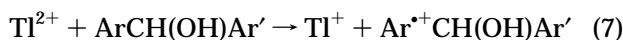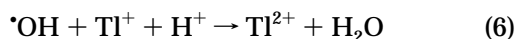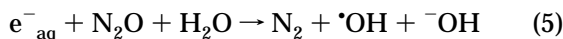(4) Baciocchi, E.; Bietti, M.; Steenken, S. *Chem. Eur. J.* **1999,** *5,* 1785–1793.

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Chart 1

H₃CO—⟨ ⟩—CH(OH)—⟨ ⟩—X

1a X = OCH₃
1b X = CH₃
1c X = H
1d X = Cl
1e X = CF₃

H₃CO—⟨ ⟩(OCH₃)—CH(OH)—⟨ ⟩—CH₃

2

H₃CO—⟨ ⟩—CH₂—⟨ ⟩—X

3a X = OCH₃
3c X = H

hydrated electron (e^-_{aq}) reacts with the peroxydisulfate anion, leading to the formation of $SO_4^{\bullet-}$ (eq 3), with $k = 1.2 \times 10^{10}$ M^{-1} s^{-1}.[6] $SO_4^{\bullet-}$ is known to react with anisole-type derivatives by electron transfer to give the corresponding radical cations (eq 4) with a rate constant $k = 5 \times 10^9$ M^{-1} s^{-1}.[4,7,8]

In the case of **2**, Tl^{2+} was also used as the oxidant, produced by irradiating N$_2$O-saturated aqueous solutions (method 2, eqs 1, 5−7):

$$e^-_{aq} + N_2O + H_2O \rightarrow N_2 + {}^{\bullet}OH + {}^-OH \quad (5)$$

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

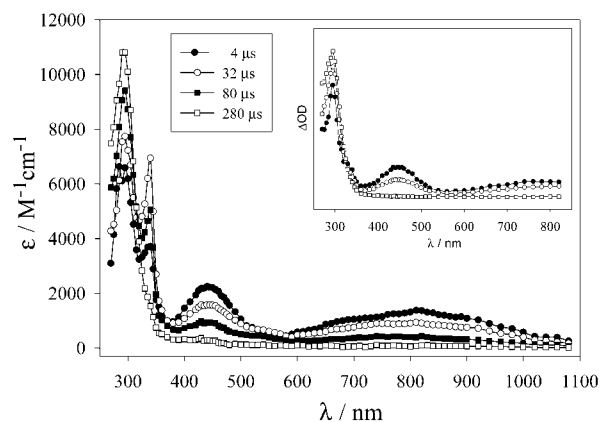$$Tl^{2+} + ArCH(OH)Ar' \rightarrow Tl^+ + Ar^{\bullet+}CH(OH)Ar' \quad (7)$$

The function of N$_2$O 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}.[9] Tl^{2+} is then produced by oxidation of Tl$^+$ by $^{\bullet}$OH (eq 6) with $k = 1.2 \times 10^{10}$ M^{-1} s^{-1}.[10] Also Tl^{2+} reacts with anisole-type derivatives by one-electron transfer to give the corresponding radical cations (eq 7) with $k \approx 5 \times 10^8$ M^{-1} s^{-1}.[7]

Product Analysis. Product analysis was carried out under acidic conditions (pH = 4.0) for substrates **1a−e** and **2** using potassium 12-tungstocobalt(III)ate, K$_5$[Co-(III)W$_{12}$O$_{40}$] (from now on indicated as Co(III)W), a genuine one-electron chemical oxidant,[11,12] to generate the radical cations. 4-Methoxy-4′-X-benzophenones (**5a−e**) and 3,4-dimethoxy-4′-methylbenzophenone were the exclusive products observed.

Product analysis of **1a** was also studied under both acidic (pH = 4.0) and basic (pH = 10.0) conditions, generating the oxidant by means of steady-state ^{60}Co γ-radiolysis. Argon-saturated aqueous solutions containing **1a** (1 mM), K$_2$S$_2$O$_8$ (0.5 mM), and 2-methyl-2-propanol (0.2 M) were irradiated at room temperature with a ^{60}Co γ-source at dose rates of 0.5 Gy s^{-1} for the time necessary to obtain a 40% conversion with respect to peroxydisulfate. 4,4′-Dimethoxybenzophenone (**5a**) was the exclusive product observed under both conditions.

Spectral Properties. Spectral information about radical cations **1$^{\bullet+}$−3$^{\bullet+}$** was obtained using the pulse radiolysis technique, generating the radical cations by reaction of **1−3** with $SO_4^{\bullet-}$, as described in eqs 1−4. As an example, in Figure 1 are displayed the time-resolved

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Figure 1. Time-resolved absorption spectra observed on reaction of $SO_4^{\bullet-}$ with **1b** (0.2 mM) at $T = 25$ °C, recorded after pulse radiolysis of an Ar-saturated aqueous solution (pH = 3.9), containing 0.1 M 2-methyl-2-propanol and 5 mM K$_2$S$_2$O$_8$, at 4 μs (filled circles), 32 μs (empty circles), 80 μs (filled squares) and 280 μs (empty squares) after the 50 ns, 10 MeV electron pulse. Inset: Time-resolved absorption spectra observed on reaction of $SO_4^{\bullet-}$ with **1b** (0.2 mM) at $T = 25$ °C, recorded after pulse radiolysis of an O$_2$-saturated aqueous solution (pH = 3.9), containing 0.1 M 2-methyl-2-propanol and 5 mM K$_2$S$_2$O$_8$, at 4 μs (filled circles), 32 μs (empty circles), and 280 μs (empty squares) after the 50 ns, 10 MeV electron pulse.

Table 1. Spectral Data for the Radical Cations of Diarylmethanols 1 and 2 and Diarylmethanes 3, Generated by Pulse Radiolysis in Aqueous Solution (pH ≈ 4.0)

radical cation	λ_{max}/nm			$\Delta OD_C/\Delta OD_B$
	A	B	C	
1a$^{\bullet+}$	290	440	980	0.81
1b$^{\bullet+}$	290	450	800	0.61
1c$^{\bullet+}$	290	450	680	0.49
1d$^{\bullet+}$	290	450	690	0.47
1e$^{\bullet+}$	290	450	560^a	<0.42
2$^{\bullet+}$	300	420	620	0.45
3a$^{\bullet+}$	300	440	960	0.39
3c$^{\bullet+}$	300	440	680	0.29

^{a} Shoulder.

absorption spectra observed on reaction of $SO_4^{\bullet-}$ with **1b** in an argon-saturated aqueous solution (pH = 3.9), recorded after 4, 32, 80, and 280 μs.

The spectrum after 4 μs (filled circles), showing three absorption bands centered around 290, 450, and 800 nm, can be reasonably assigned to **1b$^{\bullet+}$**. Interestingly, as compared to 1-(4-methoxyphenyl)alkanol radical cations, which display only two bands around 290 and 450 nm,[4] an additional band is now present. Decay of **1b$^{\bullet+}$** is accompanied by the formation of an intermediate characterized by a sharp absorption band at 340 nm and a weak absorption around 550 nm (32 μs, empty circles) which is quenched by oxygen (inset), followed by the formation of a stable product which shows a strong absorption at 295 nm (280 μs, full squares) and is unaffected by oxygen.

An analogous behavior was observed also with **1a$^{\bullet+}$**, **1c$^{\bullet+}$**, **1d$^{\bullet+}$**, and **1e$^{\bullet+}$**. However, the position of the long wavelength band of the radical cations was found to be influenced by the nature of the neutral ring substituent (Table 1).

The absorption spectrum recorded after reaction of $SO_4^{\bullet-}$ with **2** displays the characteristic UV and visible

Table 2. Rate Constants for the Uncatalyzed Decay of Radical Cations 1·+ and 2·+ Generated by Pulse Radiolysis in Aqueous Solution (pH ≤ 4), Measured at $T = 25\ °C$

radical cation[a]	$k_{dec}/s^{-1\ b}$	radical cation[a]	$k_{dec}/s^{-1\ b}$
1a·+	1.8×10^4	1d·+	1.7×10^4
1b·+	1.9×10^4	1e·+	1.8×10^4
1c·+	1.9×10^4	2·+	$6.7 \times 10^{2\ c}$

[a] Radical cations generated by method 1 from argon-saturated aqueous solutions at pH = 4.0. Dose ≈ 1 Gy/pulse. [b] Error ≤ 5%. [c] Generated by method 2 from N$_2$O-saturated aqueous solutions at pH = 3.5. Dose ≈ 1 Gy/pulse.

absorption bands of 3,4-dimethoxybenzyl alcohol radical cation centered around 300 and 420 nm[13] and a broad absorption band centered around 620 nm and can be reasonably assigned to **2·+**.

The absorption spectra of **3a·+** and **3c·+**, observed after reaction of SO$_4$·− with **3a** and **3c**, show three absorption bands corresponding to those observed for **1a·+** and **1c·+**. Decay of **3a·+** and **3c·+** is accompanied in both cases by the formation of a species characterized by a sharp absorption band at 340 nm and a weak absorption around 550 nm, which is quenched by oxygen. No stable product absorbing around 295 nm was observed in this case. The spectral data for radical cations **1·+−3·+** are collected in Table 1.

Kinetic Studies. In acidic solution, the rate of decay of the radical cations **1·+** and **2·+** was measured spectrophotometrically by following the change in optical density at the wavelengths corresponding to the UV and visible absorption maxima: 290−300, 420−450, and 600−1000 nm (see Table 1). Under these conditions the radical cations were found to decay by a first-order reaction and the same values of the rates were determined for the three absorption bands, fully supporting their assignment to the same transient species, i.e., the radical cation. The rate constants for the uncatalyzed decay of radical cations **1·+** and **2·+** are reported in Table 2.

The reactivity of radical cations **1a·+−1e·+** was studied also in alkaline solution. Under these conditions, the radical cations decay at a significantly faster rate as compared to the acidic solution, as indicated in Figure 2, displaying the time-resolved absorption spectra observed on reaction of SO$_4$·− with **1a** at pH = 9.5.[14]

Decay of **1a·+** is accompanied by the rapid formation of an intermediate characterized by a sharp absorption band at 340 nm and a broad absorption around 570 nm (26 μs, empty circles), which is quenched by oxygen, followed by the formation of a stable product that shows a strong absorption at 295 nm (332 μs, filled squares) and is unaffected by oxygen.

The decay rates of radical cations **1a·+−1e·+** were measured spectrophotometrically following the decrease in optical density at 450 nm, as a function of the concentration of −OH. Clean first-order decays and linear dependencies of the observed rates (k_{obs}) on the concentrations of added −OH were obtained. In Figure 3, the effect of [−OH] on the rate of decay of **1a·+** is displayed.

From the slope of these plots, the second-order rate constants for reaction of −OH with the radical cations (k_{OH}) were determined as $k_{OH} = 1.4 \times 10^{10}\ M^{-1}\ s^{-1}$.

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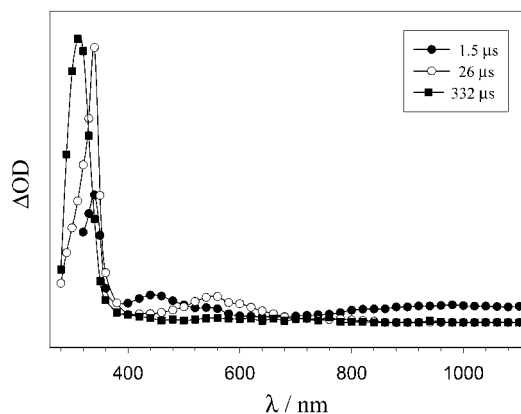
Figure 2. Time-resolved absorption spectra observed on reaction of SO$_4$·− with **1a** (0.2 mM) at $T = 25\ °C$, recorded after pulse radiolysis of an Ar-saturated aqueous solution (pH = 9.5), containing 0.1 M 2-methyl-2-propanol, 1 mM Na$_2$B$_4$O$_7$, and 5 mM K$_2$S$_2$O$_8$, at 1.5 μs (filled circles), 26 μs (empty circles), and 332 μs (empty squares) after the 50 ns, 10 MeV electron pulse.
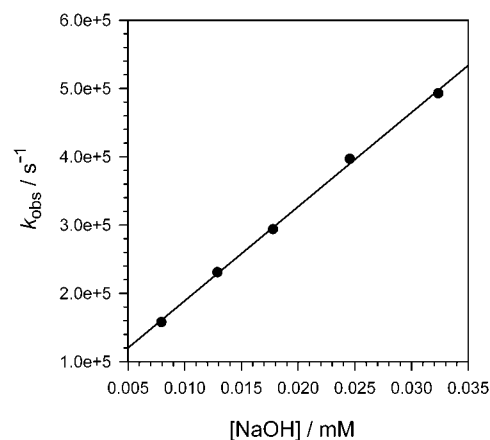

Figure 3. Effect of [−OH] on the rate of decay of **1a·+**. Slope = $1.4 \times 10^7\ mM^{-1}\ s^{-1}$, intercept = $5.1 \times 10^4\ s^{-1}$, $r^2 = 0.9987$.

Discussion

Spectral Properties. The UV−vis absorption spectra of diarylmethanol radical cations **1a·+−1e·+** (Table 1) closely resemble the spectrum of 4-methoxybenzyl alcohol radical cation, displaying two absorption bands centered at 290 and 450 nm.[4] However, the broad band in the long wavelength region is only present in the spectra of diarylmethanol radical cations. NIR absorption bands are characteristic of dimeric aromatic radical cations and have been ascribed to a charge-resonance transition.[15,16] In our case, the origin of this band can be reasonably attributed to the interaction between the neutral donor ring and the oxidized acceptor arene moieties due to strong (π,π)-orbital overlap, an example of intramolecular charge resonance (CR) absorption.[17] The intramolecular nature of this interaction is supported by the observation that the relative intensity of the CR band compared to

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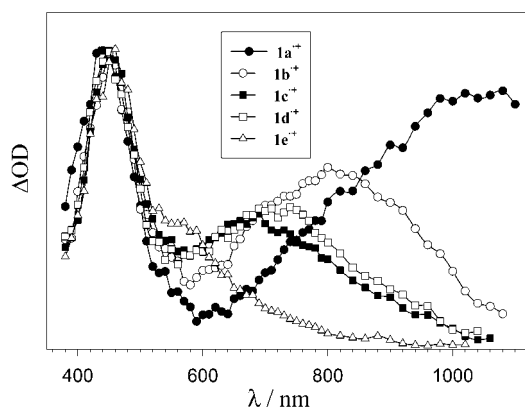
Figure 4. Time-resolved vis−NIR absorption spectra of **1a**[•+]−**1e**[•+] observed on reaction of $SO_4^{•-}$ with **1a**−**e** (0.2 mM) at $T =$ 25 °C, recorded after pulse radiolysis of an Ar-saturated aqueous solution (pH = 3.9−4.1), containing 0.1 M 2-methyl-2-propanol and 5 mM $K_2S_2O_8$, at ca. 4 μs after the 50 ns, 10 MeV electron pulse.

that of the UV and visible bands does not increase with increasing substrate concentration in the range 0.1−0.4 mM.

The observation of a CR band in diarylmethanol radical cations indicates that there must be sufficient overlap between the orbitals involved in the interaction of the two aromatic rings, even though the geometry of the system does not fulfill the requirement of a cofacial arrangement between donor and acceptor with an interplanar separation equal to or shorter than the van der Waals contacts necessary for efficient charge transfer and optimum electronic coupling.[16,18] The attribution of the broad long wavelength band to an intramolecular CR interaction is further supported by the effect of the neutral ring substituent on the position and intensity of this band (Table 1). In Figure 4 are displayed the vis−NIR spectra of **1a**[•+]−**1e**[•+].

The position of the band centered around 450 nm is almost unaffected by varying the neutral ring substituent; however, an increase in the electron-donor properties of these substituents results in a significant red shift of the CR band and in an increase of the relative intensity of the CR band with respect to the 450 nm band.

Charge resonance between an aromatic donor and a radical cation acceptor may be interpreted in terms of the classical Mulliken charge transfer theory.[15,20] Along this line, a good linear correlation is obtained when the energy of the CR band (E_{CR}) for **1a**[•+]−**1e**[•+] is plotted against the difference in ionization potentials ($IP_D − IP_A$) between 4-$XC_6H_4CH_3$ and 4-$CH_3OC_6H_4CH_3$,[21] taken as models of the two aromatic moieties of **1a**−**1e**. E_{CR} increases linearly by increasing the electron-withdrawing properties of the donor ring substituent (IP_D) (Figure 5).

Figure 5. Plot of the CR band energy (E_{CR}) vs the difference in ionization potentials ($IP_D − IP_A$) between 4-$XC_6H_4CH_3$ (IP_D) (taken from refs 22 and 23). and 4-$CH_3OC_6H_4CH_3$ (IP_A) (8.18 eV, taken from ref 22). $r^2 = 0.992$.

In agreement with the theory, an analogous effect is observed with **2**[•+], which contains two methoxy groups in the charged acceptor ring, i.e., by lowering IP_A. Accordingly, the CR absorption band is now centered at 620 nm, a value which is significantly blue-shifted with respect to that observed for the corresponding monomethoxylated diarylcarbinol **1b**[•+] (800 nm).

A CR interaction is also observed with diarylmethane radical cations **3a**[•+] and **3c**[•+], the CR absorption band corresponding to that observed for **1a**[•+] and **1c**[•+] (Table 1), indicating that the position of this band is not affected by the presence of an α-OH group.

Reactivity. In acidic solution, decay of radical cations **1a**[•+]−**1e**[•+] is accompanied by the formation of an intermediate characterized by a sharp absorption band at 340 nm and a weak absorption around 550 nm, which is quenched by oxygen followed by the formation of a stable product that shows a strong absorption at 295 nm and is unaffected by oxygen. A similar situation was also observed in basic solution, where, however, the visible absorption band of the intermediate formed after decay of the radical cations is now centered at 570 nm and is significantly more intense than that observed in acidic solution. On the basis of these observations, the results of product analysis, indicating the formation of benzophenones as exclusive reaction products, and literature data,[24,25] the intermediate formed after decay of **1a**[•+]−**1e**[•+] can be reasonably assigned to the ketyl radical 4-$MeOC_6H_4C(•)OHC_6H_4X$ (**4**[•]) in acidic solution and to the corresponding ketyl radical anion 4-$MeOC_6H_4C(•)O(^-)$-C_6H_4X (**4**[•−]) in basic solution, while the stable product is assigned in both cases to the benzophenone 4-$MeOC_6H_4$-COC_6H_4X (**5**). The attribution of the intermediates to the ketyl radical **4**[•] and to the ketyl radical anion **4**[•−] is confirmed by comparison with the spectra of **4a**[•] and **4a**[•−] (Figure 6), generated independently after pulse radiolysis of an argon-saturated aqueous solution containing (4-$MeOC_6H_4$)$_2$CO (**5a**) and 2-methyl-2-propanol (to scavenge •OH, as described in eq 2).
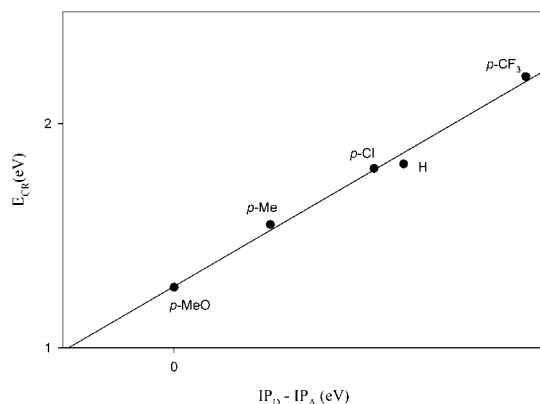
(17) A vis−NIR CR band has been observed for the radical cations of diphenylmethane, generated by γ-radiolysis of a glassy isopentane−butyl chloride mixture at 77 K[18] and of 1,3-bis(aryl)propanes generated by pulse radiolysis in 1,2-dichloroethane.[19]

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(21) The ionization potentials of 4-$CH_3OC_6H_4CH_3$ (8.18 eV), 4-$CH_3C_6H_4$-CH_3 (8.44 eV), $C_6H_5CH_3$ (8.82 eV), and 4-$ClC_6H_4CH_3$ (8.69 eV) are taken from ref 22. The ionization potential of 4-$CF_3C_6H_4Me$ (9.13 eV) has been estimated by the correlation of the ionization potential of ring-substituted toluenes vs Hammett σ values.[23]
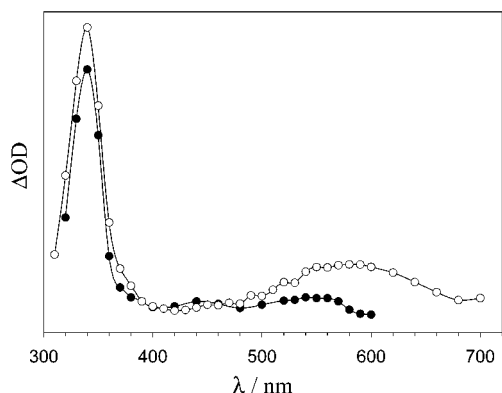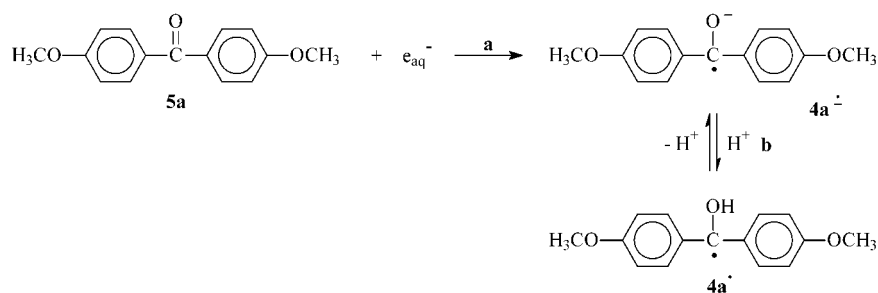
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Scheme 1

Figure 6. Time-resolved absorption spectra recorded after pulse radiolysis of an Ar-saturated aqueous solution containing 0.05 mM (4-MeOC$_6$H$_4$)$_2$CO (**5a**), 1 M 2-methyl-2-propanol, 1 mM KH$_2$PO$_4$ (pH = 5.0), or 1 mM Na$_2$B$_4$O$_7$ (pH = 11.0) and 20% MeCN (to solubilize **5a**) at 4 μs after the 50 ns, 10 MeV electron pulse. pH = 5.0 (filled circles), pH = 11.0 (empty circles).

Scheme 2
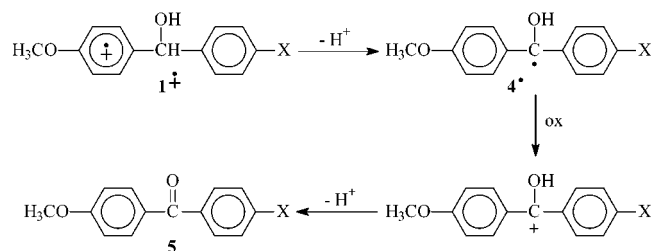
4a$^{\bullet-}$ is formed after reaction of **5a** with e$^-_{aq}$ (Scheme 1, path a) followed, in acidic solution, by rapid protonation of the ketyl radical anion to give **4a$^\bullet$** (path b).[13,26,27]

In acidic solution, decay of **1a$^{\bullet+}$**–**1e$^{\bullet+}$**, which is also unaffected by oxygen, can thus be attributed to deprotonation from the diaryl substituted carbon, leading to the corresponding carbon-centered radical **4$^\bullet$**, which is then oxidized in the reaction medium, finally leading to **5** (Scheme 2), a typical reaction of arylalkanol radical cations.[4,29]

The deprotonation rate constants for **1a$^{\bullet+}$**–**1e$^{\bullet+}$** are almost identical ($k \approx 1.8 \times 10^4$ s^{-1}) and close to the value measured for 4-methoxybenzyl alcohol radical cation (k

$= 7.5 \times 10^3$ s^{-1}, statistically corrected for the number of α-hydrogen atoms),[4] indicating that the effect of the additional aromatic ring on the deprotonation rate constant is small and consequently that of the ring substituents are negligible. This observation is somewhat surprising, as one would have expected a larger increase in deprotonation rate due to the higher stability of the diarylcarbinyl radical as compared to the arylcarbinyl one.[30] However, deprotonation reactions of alkylaromatic radical cations have been described to proceed through an early transition state.[4,24,32,33]

Decay of **2$^{\bullet+}$**, assigned on the basis of product studies to C$_\alpha$-H deprotonation, is much slower than that of **1b$^{\bullet+}$**, a result that can be explained with the increased stability of the radical cation and in line with the relative deprotonation rate of 4-methoxy and 3,4-dimethoxybenzyl alcohol radical cations.[4,13]

Decay of diarylmethane radical cations **3a$^{\bullet+}$** and **3c$^{\bullet+}$** is assigned to C–H deprotonation, as also in this case the formation of the diarylmethyl radical characterized by a sharp absorption band at 340 nm and a weak absorption around 550 nm was observed.[24,25,34]

The values of k_{OH^-} measured for the reactions of **1a$^{\bullet+}$**–**1e$^{\bullet+}$** with $^-$OH, are all very similar ($\approx 1.4 \times 10^{10}$ M^{-1} s^{-1}) and in agreement with values determined previously for 1-(4-methoxyphenyl)alkanol radical cations,[4,35] indicating interaction of $^-$OH with the α-OH function of the radical cation, as described in Scheme 3.

The radical cation undergoes diffusion-controlled O–H deprotonation to give a radical zwitterion which, directly or through the intermediacy of a benzyloxyl radical,[5] undergoes a 1,2-H atom shift to give the ketyl radical **4$^\bullet$**. This radical is then deprotonated to give the corresponding radical anion (**4$^{\bullet-}$**), which is finally oxidized to benzophenone **5**. It might also be suggested that the radical zwitterion undergoes $^-$OH-induced C$_\alpha$-H deprotonation, directly leading to the ketyl radical anion, which accordingly was observed spectroscopically; however, such an hypothesis seems unlikely, since it should lead to an overall reaction that is second-order in base, which has not been observed experimentally. Moreover, in the

(26) Konya, K. G.; Paul, T.; Lin, S.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **2000**, *122*, 7518–7527.

(27) In both ethanol and 2-propanol, a pK_a = 9.25 has been determined for (C$_6$H$_5$)$_2$CH($^\bullet$)OH.[28]

(28) Autrey, T.; Kandanarachchi, P.; Franz, J. A. *J. Phys. Chem. A* **2001**, *105*, 5948–5953.

(29) Baciocchi, E.; Belvedere, S.; Bietti, M.; Lanzalunga, O. *Eur. J. Org. Chem.* **1998**, *1*, 299–302. Walling, C.; El-Taliawi, G. M.; Zhao, C. *J. Org. Chem.* **1983**, *48*, 4914–4917. Trahanovsky, W. S.; Cramer, J. *J. Org. Chem.* **1971**, *36*, 1890–1893.

(30) The difference in stability between C$_6$H$_5$CH$_2^\bullet$ and (C$_6$H$_5$)$_2$CH$^\bullet$ is 4 kcal mol^{-1}. However, this difference is likely to decrease in the presence of an OH group at the radical center.[31]

(31) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.

(32) Amatore, C.; Kochi, J. K. *Adv. Electron-Transfer Chem.* **1991**, *1*, 55–148.

(33) A role may be also played by stereoelectronic effects, since in the presence of a CR interaction between the two aromatic rings (see text) it is more difficult to reach the conformation required for deprotonation, where the scissile C–H bond is collinear with the aromatic π system.[3b]

(34) No kinetic studies were carried out for these radical cations.

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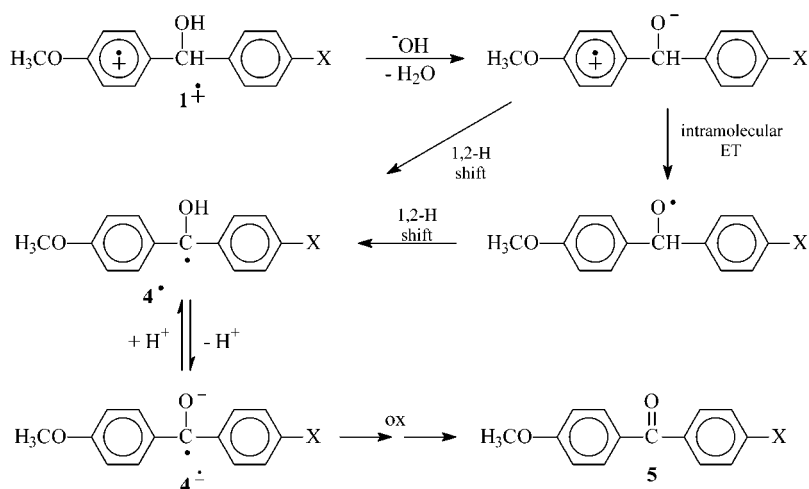
Scheme 3

presence of $^-$OH, deprotonation of **4·** to give the ketyl radical anion is expected to be a relatively fast process.[36]

Conclusions

The absorption spectra of ring-methoxylated diarylmethane and diarylmethanol radical cations display, in addition to the characteristic UV and visible bands of methoxybenzene radical cations, a broad band in the vis—NIR region of the spectrum. This band has been assigned to an intramolecular charge resonance (CR) interaction between the donor and acceptor rings on the basis of the observation that the relative intensity of the CR band to that of the UV and visible bands does not increase with increasing substrate concentration and by the effect of the ring substituents on the position and intensity of this band. In acidic solution the radical cations undergo C—H deprotonation, leading to the corresponding diarylmethyl radicals. In the case of diarylmethanol radical cations, the intermediate ketyl radical is further oxidized to give the corresponding benzophenones, as evidenced by both spectroscopic and product studies. In basic solution, diarylmethanol radical cations undergo $^-$OH-induced deprotonation from the α-OH group, a typical reaction of 1-(4-methoxyphenyl)alkanol radical cations.

Experimental Section

Materials. Potassium peroxydisulfate, sodium hydroxide, disodium tetraborate decahydrate, and 2-methyl-2-propanol were of the highest commercial quality available. Milli-Q-filtered water was used for all solutions. 4,4′-Dimethoxybenzhydrol (**1a**) was used as received. 4,4′-Dimethoxydiphenylmethane (**3a**) and 4-methoxydiphenylmethane (**3c**) were available from a previous work.[24]

4-Methoxybenzhydrol (**1c**)[37] was prepared by reduction of 4-methoxybenzophenone with NaBH$_4$, purified by column chromatography (silica gel, eluent hexane/ethyl acetate 5:1).

4-Chloro-4′-methoxybenzhydrol (**1d**),[38] 4-methoxy-4′-methylbenzhydrol (**1b**),[39] and 4-methoxy-4′-trifluoromethylbenzhy-drol (**1e**)[39] were prepared by reaction of 4-methoxyphenylmagnesium bromide with 4-chlorobenzaldehyde, 4-methylbenzaldehyde, and 4-trifluoromethylbenzaldehyde, respectively.

3,4-Dimethoxy-4′-methylbenzhydrol (**2**) was synthesized in a similar way by reaction of 3,4-dimethoxyphenylmagnesium bromide with 4-methylbenzaldehyde. ^{1}H NMR: δ 7.27—7.12 (m, 4H, ArH), 6.93—6.78 (m, 3H, ArH), 5.76 (s, 1H, CH), 3.85 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 2.33 (s, 3H, CH_3). MS: m/z (rel intensity) M$^+$ 258, 185, 139 (100), 119, 91, 77.

Co(III)W was prepared using the literature procedure,[12] with some modifications.[40]

Reaction Products. All products were identified by comparison with authentic specimens. 4,4′-dimethoxybenzophenone (**5a**) and 4-methoxybenzophenone (**5c**) were commercially available. 4-Methoxy-4′-methylbenzophenone (**5b**),[41] 4-chloro-4′-methoxybenzophenone (**5d**),[38] 4-methoxy-4′-trifluoromethylbenzophenone (**5e**),[42] and 3,4-dimethoxy-4′methylbenzophenone [^{1}H NMR: δ 7.67—7.35 (m, 7H, ArH), 3.96 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 2.44 (s, 3H, CH_3)] were prepared by oxidation of the corresponding alcohols with chromic acid or Jones reagent.

Product Analysis. γ-Radiolysis. Argon-saturated aqueous solutions containing **1a** (1 mM), K$_2$S$_2$O$_8$ (0.5 mM), and 2-methyl-2-propanol (0.2 M) both in acidic (pH = 4.0) and basic (pH = 10.0) solution were irradiated at room temperature with a ^{60}Co γ-source at dose rates of 0.5 Gy s^{-1} for the time necessary to obtain a 40% conversion with respect to peroxydisulfate. 4,4′-Dimethoxybenzophenone was the exclusive product observed under both acidic and basic conditions. Reaction products were identified by GC—MS and ^{1}H NMR by comparison with authentic specimens. Yields were determined by ^{1}H NMR (using bibenzyl as the internal standard) and referred to the starting material. A good material balance (>95%) was observed in all the experiments.

Oxidations with Co(III)W. The oxidant Co(III)W (2 mM) and the substrate (2 mM) were magnetically stirred in 10 mL of an argon-degassed 50 mM sodium tartrate buffer solution (pH = 4.0), at 50 °C. After 48 h (6 h in the oxidation of **2**), the products of the reaction were extracted with ethyl ether and dried over anhydrous Na$_2$SO$_4$. 4-Methoxy-4′-X-benzophenones (**5a**—**5e**) and 3,4-dimethoxy-4′-methylbenzophenone were the exclusive products observed.[43] Yields are as follows: **5a**, 27%; **5b**, 24%; **5c**, 22%; **5d**, 19%; 3,4-dimethoxy-4′-methylbenzophenone, 38%.

(36) The equilibrium between the ketyl radical $^-$O$_2$CC$_6$H$_4$CH(·)OH and the corresponding radical dianion $^-$O$_2$CC$_6$H$_4$CH(·)O$^-$ was found to be catalyzed by secondary phosphate with $k \approx 10^8$ M^{-1} s^{-1}.[26] Thus, the spectra displayed in Figure 2 show only the conversion of **1a·$^+$** into the corresponding ketyl radical anion, since this process is significantly slower than the equilibrium described in Scheme 1.

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(41) Atkinson, G. E.; Fischer, P. M.; Chan, W. C. *J. Org. Chem.* **2000**, *65*, 5048—5056.

(42) Uehara, F.; Sato, M.; Kaneko, C.; Kurihara, H. *J. Org. Chem.* **1999**, *64*, 1436—1441.

(43) Due to the lower solubility of **1e** as compared to **1a—d**, the exclusive reaction product **5e** was not quantitatively determined.

Pulse Radiolysis. The pulse radiolysis experiments were performed using a 10 MeV electron linear accelerator that supplied 50 ns pulses with doses such that $1-3$ μM radicals were produced. Experiments were performed at room temperature using argon- or oxygen-saturated aqueous solutions containing the substrate ($0.05-1.0$ mM), peroxydisulfate ($5-10$ mM), and 2-methyl-2-propanol ($0.1-1.0$ M). The pH of the solutions was adjusted with NaOH or HClO$_4$, and for the experiments carried out at pH > 9, 1 mM sodium tetraborate was added to avoid undesired pH variations upon irradiation. A flow system was employed in all the experiments. The observed rates (k_{obs}) were obtained by averaging $6-12$ values, each consisting of an average of $5-15$ shots and were reproducible to within 5%.

The second-order rate constants for reaction of the radical cations with $^-$OH (k_{OH^-}) were obtained from the slopes of the plots of k_{obs} vs the concentration of NaOH.

The ketyl radical and radical anion, (4-MeOC$_6$H$_4$)$_2$C($^{\bullet}$)OH (**4a$^{\bullet}$**) and (4-MeOC$_6$H$_4$)$_2$C($^{\bullet}$)O$^-$ (**4a$^{\bullet -}$**), were generated after pulse radiolysis of an argon-saturated aqueous solution (pH = 5.0 and 11.0, respectively) containing 0.05 mM (4-MeOC$_6$H$_4$)$_2$CO (**5a**), 1 M 2-methyl-2-propanol, 1 mM Na$_2$B$_4$O$_7$, and 20% MeCN (to solubilize **5a**).