



⁻OH-Induced shift from carbon to oxygen acidity in the side-chain deprotonation of 2-, 3- and 4-methoxybenzyl alcohol radical cations in aqueous solution: results from pulse radiolysis and DFT calculations

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Abstract—DFT calculations have been carried out for 2-, 3- and 4-methoxybenzyl alcohol radical cations ($\mathbf{1}^{\cdot+}$, $\mathbf{3}^{\cdot+}$ and $\mathbf{4}^{\cdot+}$, respectively) and the α -methyl derivatives $\mathbf{2}^{\cdot+}$ and $\mathbf{5}^{\cdot+}$ using the UB3LYP/6-31G(d) method. The theoretical results have been compared with the experimental rate constants for deprotonation of $\mathbf{1}^{\cdot+}$ – $\mathbf{5}^{\cdot+}$ under acidic and basic conditions. In acidic solution, the decay of $\mathbf{1}^{\cdot+}$ – $\mathbf{5}^{\cdot+}$ proceeds by cleavage of the C–H bond, while in the presence of ⁻OH all the radical cations undergo deprotonation from the α -OH group. This pH-dependent change in mechanism has been interpreted qualitatively in terms of simple frontier molecular orbital theory. The ⁻OH induced α -O–H deprotonation is consistent with a charge controlled reaction, whereas the C–H deprotonation, observed when the base is H₂O, appears to be affected by frontier orbital interactions. © 2003 Elsevier Science Ltd. All rights reserved.

We have recently shown the existence of a pH-dependent mechanistic dichotomy for the deprotonation of 4-methoxybenzyl alcohol radical cation in aqueous solution.¹ Accordingly, in neutral and acidic solutions 4-MeOC₆H₄CH₂OH⁺ undergoes the expected C–H deprotonation (Scheme 1, path a), whereas in basic solution (pH=10), the reaction is initiated by deprotonation of the OH group (Scheme 1, path b). A benzyloxy radical is formed, probably through an intermediate radical zwitterion. In other words, 4-MeO-C₆H₄CH₂OH⁺ displays carbon acidity when the base is water and oxygen acidity when the base is ⁻OH.

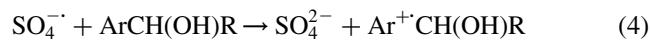
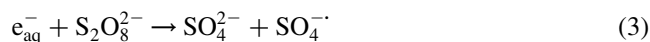
To shed some light on this mechanistic dichotomy we have now carried out DFT calculations leading to charge distributions, frontier orbital coefficients and spin densities for 2-, 3- and 4-methoxybenzyl alcohol radical cations ($\mathbf{1}^{\cdot+}$, $\mathbf{3}^{\cdot+}$ and $\mathbf{4}^{\cdot+}$, respectively) and the α -methyl derivatives $\mathbf{2}^{\cdot+}$ and $\mathbf{5}^{\cdot+}$. To compare the results of these calculations with the deprotonation rates of the radical cations, we have also carried out a kinetic study of the deprotonation of $\mathbf{1}^{\cdot+}$ – $\mathbf{3}^{\cdot+}$ under acidic (C–H deprotonation) and basic (O–H deprotonation) conditions, by using the pulse radiolysis

technique. The deprotonation rate constants for $\mathbf{4}^{\cdot+}$ and $\mathbf{5}^{\cdot+}$ were available from previous studies (Chart 1).^{1b}

1. Results

1.1. Generation and spectral properties of the radical cations

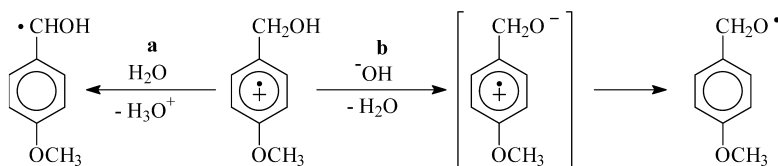
Radical cations of substrates **1**–**5** were generated in aqueous solution by means of radiation chemical techniques (pulse radiolysis and steady-state ⁶⁰Co γ -radiolysis) employing sulfate radical anion (SO₄⁻) as the oxidant (method 1; Eqs. (1)–(4)):



The hydroxyl radical ([•]OH) is scavenged by 2-methyl-2-propanol (Eq. (2)) with $k=6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$,² while the hydrated electron (e_{aq}^-) reacts with the peroxydisulfate anion leading to the formation of SO₄⁻ (Eq. (3)), with $k=1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.³ SO₄⁻ is known to react with anisole-

Keywords: radical cation; DFT calculations; deprotonation; pulse radiolysis; oxygen acidity; benzyl alcohol.

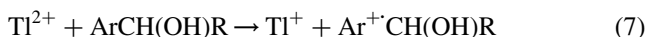
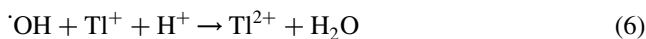
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Scheme 1.

type derivatives by electron transfer to give the corresponding radical cations (Eq. (4)) with rate constants $k \approx 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.^{3–5}

Alternatively, Ti^{2+} was used as the oxidant, produced by irradiating N_2O saturated aqueous solutions (method 2; Eqs. (1), (5)–(7)):



The function of N_2O is to scavenge e_{aq}^- , leading to the formation of an additional hydroxyl radical (Eq. (5)), with $k = 9.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.⁶ Ti^{2+} is then produced by oxidation of Ti^+ by $\cdot\text{OH}$ (Eq. (6)) with $k = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.^{7,8} Also Ti^{2+} reacts with anisole-type derivatives by one-electron transfer to give the corresponding radical cations (Eq. (7)) with $k \approx 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.³

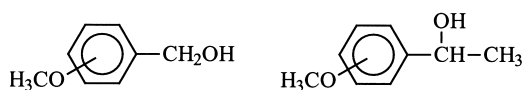
The radical cations showed the characteristic UV and visible absorption bands centered around 285–290 and 420–450 nm.^{1b,3,5} The spectral data for radical cations $1^+–5^+$ are reported in Table 1.

1.2. Product studies

Product analysis of the reactions of radical cations $1^+–5^+$ both in acidic (pH=4.0) and basic (pH=10.0) solution was carried out by steady state γ -radiolysis, using method 1 to produce the radical cations. Argon-saturated aqueous solutions containing 1 mM substrate, 0.5 mM $\text{K}_2\text{S}_2\text{O}_8$ and 0.2 M 2-methyl-2-propanol 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. The oxidation of compounds **1–5** led in all cases to the corresponding methoxylated benzaldehyde (from **1**, **3** and **4**) or acetophenone (from **2** and **5**) as main reaction product, both under acidic and basic conditions.

1.3. Kinetic studies

1.3.1. In acidic solution. The rates of decay of radical cations $1^+–3^+$ were measured by monitoring the pro-



1: 2-OCH₃
3: 3-OCH₃
4: 4-OCH₃

2: 2-OCH₃
5: 4-OCH₃

Chart 1.

duction of H^+ at pH=3.5, using the ac-conductance technique or alternatively spectrophotometrically by measuring the decrease in optical density at 420 nm (1^+ and 2^+) or 450 nm (3^+). For radical cation generation, method 2 was preferred to method 1 since with the former is avoided the presence of radicals such as $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$, formed by hydrogen atom abstraction from 2-methyl-2-propanol by $\cdot\text{OH}$ (Eq. (2)), which limits the lifetime of the radical cations.⁹

Under these conditions the radical cations were found to decay by a first-order reaction which, on the basis of the product analysis results, is assigned to C–H deprotonation from the benzylic carbon, as described in Scheme 1, path a. These values are similar to those measured analogously for 4^+ and 5^+ , whose behavior as carbon acids has already been assessed.^{1b} The values of the rate constants for the uncatalyzed decay of radical cations $1^+–5^+$ are reported in Table 2, column 2.

1.3.2. In the presence of ^-OH . By monitoring the decay of radical cations $1^+–5^+$ at 420–450 nm a significant increase in rate was observed when ^-OH was added to the solution, and by plotting the observed rates for decay (k_{obs}) vs. concentration of added base, a linear dependence was observed for all radical cations. From the slopes of these plots, the second-order rate constants for reaction of ^-OH with the radical cations ($k_{-\text{OH}}$) were determined. The rate constants thus obtained are shown in column 3 of Table 2. All the rate constants appear to be diffusion controlled ($k_{-\text{OH}}$ between 1.2 and $1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$), a behavior which is indicative of O–H deprotonation as previously discussed.¹

1.4. DFT calculations

Hybrid density functional theory (DFT) calculations with unrestricted MO formalism [UB3LYP/6-31G(d) method] were carried out for radical cations $1^+–5^+$. This method was used because, contrarily to ROHF methods, it takes spin polarization into account, and avoids the artifact, typical of UHF methods, of spin contamination. Accordingly, the results provided for radical cations have been found to be very reliable.¹⁰ Since in the case of the radical cations 2^+ and 5^+ the benzylic carbon is a stereogenic center, calculations were carried out for the corresponding *R* enantiomers. The global energy minimum structures for radical cations $1^+–5^+$ thus obtained are schematically reported in Chart 2.

In all cases, the most stable conformation involves the methoxy group coplanar with the aromatic ring and oriented as shown in Chart 2. In the case of 1^+ , 3^+ and 4^+ , the benzylic OH group is eclipsed with the aromatic ring

Table 1. Spectral data for the radical cations generated by pulse radiolysis in aqueous solution (pH 3.5–4.0) from the corresponding methoxybenzyl alcohol derivatives **1–5**

Substrate	Radical cation	Method of generation ^a	λ_{\max} (nm)	ϵ_{\max} ($M^{-1} \text{ cm}^{-1}$)
2-MeOC ₆ H ₄ CH ₂ OH	1 ^{•+}	1 (2)	285	5100 (5200)
			420	2300 (2100)
2-MeOC ₆ H ₄ CH(OH)CH ₃	2 ^{•+}	1	285	6500
			420	2400
3-MeOC ₆ H ₄ CH ₂ OH	3 ^{•+}	1 (2)	285	5000 (5600)
			450	2200 (2100)
4-MeOC ₆ H ₄ CH ₂ OH	4 ^{•+}	1	290	9000
			450	3400
4-MeOC ₆ H ₄ CH(OH)CH ₃	5 ^{•+}	1	290	10000
			440	3400

^a For background on the methods of generation of the radical cations see text. For the determination of the extinction coefficients: method 1, $G(\text{radical cation})=G(\text{SO}_4^{\cdot-})=3.0 \times 10^{-7} \text{ mol J}^{-1}$; method 2, $G(\text{radical cation})=G(\text{OH})=6.0 \times 10^{-7} \text{ mol J}^{-1}$. In both cases, the pH of the solutions was adjusted with HClO₄ and doses of ≈ 4 Gy/pulse were employed.

(dihedral angle $\varphi=0^\circ$), whereas, in the case of **2**^{•+} and **5**^{•+}, it is slightly below the plane of the aromatic ring (dihedral angles $\varphi=16^\circ$ and 13° , respectively).

Theoretical data, useful for the discussion of experimental results, namely the square of the β LUMO coefficients for the benzylic C–H and O–H hydrogen atoms, the β LUMO energy, the Mulliken atomic charges of the benzylic C–H and O–H hydrogen atoms and the atomic spin densities for the benzylic C–H hydrogen atoms, have been collected in Table 3. All of these data have been obtained by UB3LYP/6-31G(d) calculations on the most stable conformation of the radical cations **1**^{•+}–**5**^{•+}.¹¹

2. Discussion

The results of kinetic and product studies show that in acidic solution the decay of radical cations **1**^{•+}–**5**^{•+} proceeds by cleavage of the C α –H bond leading, via an intermediate methoxy- α -hydroxybenzylic radical, to the pertinent methoxybenzaldehyde or methoxyacetophenone. In the presence of [–]OH instead, all the radical cations react with [–]OH at a diffusion controlled rate, a clear indication that in the [–]OH-induced deprotonation of **1**^{•+}–**5**^{•+} the reaction center is the

Table 2. Rate constants for the uncatalyzed (k) and [–]OH-catalyzed (k_{OH}) decay of radical cations **1**^{•+}–**5**^{•+} generated by pulse radiolysis in aqueous solution, measured at $T=25^\circ\text{C}$

Radical cation	k (s^{-1}) ^a	k_{OH} ($M^{-1} s^{-1}$) ^b
1 ^{•+}	5.7×10^{3c} 5.9×10^{3d}	1.6×10^{10}
2 ^{•+}	7.3×10^{2c} 7.7×10^{2d}	1.3×10^{10}
3 ^{•+}	9.6×10^{2c} 1.1×10^{3d}	1.6×10^{10}
4 ^{•+}	1.5×10^{4c} 1.8×10^{4e}	1.2×10^{10}
5 ^{•+}	7.0×10^{3c} 9.0×10^{3e}	1.4×10^{10}

^a The radical cations were generated by method 2 at pH ≈ 3.5 .

^b The radical cations were generated by method 1 (dose ≤ 5 Gy/pulse).

^c Monitored by following the increase in conductance: dose ≤ 0.5 Gy/pulse.

^d Monitored by following the decay of optical absorption at 420–450 nm: dose ≈ 1 Gy/pulse.

^e Radical cations generated by method 1 from argon-saturated aqueous solutions at pH=4.0: dose ≈ 1 Gy/pulse.

α -OH group itself. In other words, these radical cations, which in water display the expected carbon acidity, in the presence of a strong base such as [–]OH become oxygen acids, undergoing rate-determining O–H deprotonation as the first step of the decay process, in full agreement with our previous conclusions for 1-(4-methoxyphenyl)alkanol radical cations.¹

This pH-dependent change in mechanism can be interpreted qualitatively in terms of simple frontier molecular orbital (FMO) theory,¹² as we should deal with reactions characterized by a very early transition state.¹³ Moreover, very similar reduction potentials are foreseeable for **1**^{•+}–**5**^{•+} (see for example Table 3 for the β LUMO energies of **1**^{•+}–**5**^{•+}). According to FMO theory, if reactions with the same steric requirements are compared, the interaction energy between two reactants is dominated by two terms: the Coulombic term and the frontier orbital term. If the first term is the most important the reaction is charge controlled, whereas if the second one dominates, the reaction is orbital controlled. Considering the deprotonation of **1**^{•+}–**5**^{•+} promoted by the two bases [–]OH and H₂O, there is no doubt that in the reaction with [–]OH, a base having a net negative charge, the Coulombic term will be greater than the corresponding term for the reaction with H₂O. The O–H deprotonation of **1**^{•+}–**5**^{•+} observed in the presence of [–]OH is consistent with a charge controlled reaction as the Mulliken charges reported in Table 3 show that the O–H hydrogens bear an amount of positive charge more than

Table 3. Mulliken atomic charges of the benzylic C–H and O–H hydrogen atoms (Q_{CH} and Q_{OH}), square of the β LUMO coefficients for the benzylic C–H and O–H hydrogen atoms (c_{CH}^2 and c_{OH}^2), atomic spin densities for the benzylic C–H hydrogen atoms (ρ_{CH}) and β LUMO energy ($E_{\beta\text{LUMO}}$) for **1**^{•+}–**5**^{•+}, at the UB3LYP/6-31G(d) level of theory

Radical cation	Q_{CH}	Q_{OH}	c_{CH}^2 ^a	c_{OH}^2 ^a	ρ_{CH}	$E_{\beta\text{LUMO}}$ (a.u.)
1 ^{•+}	0.194	0.435	1.70×10^{-2}	8×10^{-10}	0.024	–0.34220
2 ^{•+}	0.180	0.427	1.36×10^{-2}	3.8×10^{-5}	0.020	–0.33992
3 ^{•+}	0.192	0.435	8.56×10^{-3}	1×10^{-10}	0.010	–0.34022
4 ^{•+}	0.202	0.437	2.25×10^{-2}	4×10^{-10}	0.034	–0.33626
5 ^{•+}	0.185	0.428	1.71×10^{-2}	8.7×10^{-5}	0.027	–0.33403

^a Owing to the use of a split-valence basis set the square of the coefficients of the β LUMO for CH and OH hydrogen atoms reported in the table are actually the sum of the square of the coefficients of the inner and outer s orbitals.

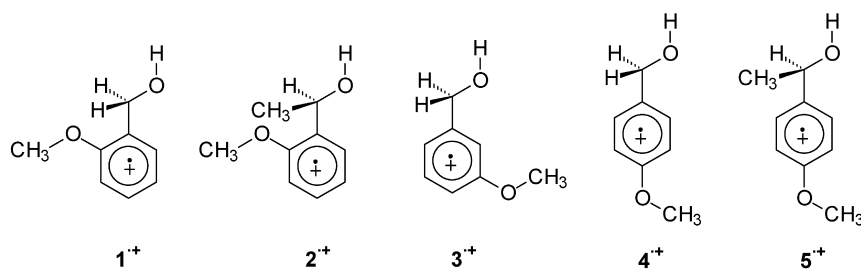


Chart 2.

double with respect to the corresponding benzylic C–H hydrogens. Calculations also show that there is no significant influence of the position of the methoxy group upon the O–H Mulliken charge, which means that the various radical cations should exhibit the same kinetic acidity. This conclusion, however, cannot be tested experimentally as the rates of ^-OH -induced deprotonation are diffusion controlled in all cases.

When we pass from ^-OH to H_2O as the base, the radical cation deprotonation reaction concerns the $\text{C}_\alpha\text{--H}$ bond and we suggest that the reaction is now governed by frontier orbital interactions. In order to evaluate such interactions, we must consider that we are using an unrestricted formalism where the MOs are divided in two sets, α and β , that can be occupied, respectively, by α and β electrons. Of course, in this formalism, each MO can only contain one electron. Since our system involves the interaction of an electrophilic radical with an electron donor, the traditional SOMO–HOMO interaction illustrated in Figure 1a must be translated into two interactions: $\alpha\text{HOMO--}\alpha\text{HOMO}$ and $\beta\text{HOMO--}\beta\text{LUMO}$ (Fig. 1b).

The first of the two interactions can be neglected since it involves filled orbitals, whereas the second will be the dominant one. Thus, in a series of electrophilic radicals reacting with the same nucleophile, the frontier orbital term is dependent on the magnitude of the square of the coefficients of the βLUMO of the radicals and inversely proportional to the energy difference between the βLUMO of the electrophilic radical and the βHOMO of the nucleophile (Eq. (8)).

$$\Delta E_{\text{FO}} \propto \frac{c_{\beta\text{LUMO}(\text{elec})}^2}{E_{\beta\text{LUMO}(\text{elec})} - E_{\beta\text{HOMO}(\text{nuc})}} \quad (8)$$

If one considers the βLUMO energies of the radical cations $1^+ \text{--} 5^+$ in Table 3, even though the energies of Kohn–Sham orbitals used in DFT calculations do not have a strict physical meaning (for example there is no equivalent of Koopmans' theorem),¹¹ it appears that they are quite similar with a maximum deviation of ± 0.003 a.u. from the average value of -0.339 a.u. Thus, in the reaction with water the HOMO–LUMO gap is so large as to be practically constant along the series of the radical cations $1^+ \text{--} 5^+$,¹⁴ and Eq. (8) reduces to Eq. (9).

$$\Delta E_{\text{FO}} \propto c_{\beta\text{LUMO}(\text{elec})}^2 \quad (9)$$

As the c_{OH}^2 term for $1^+ \text{--} 5^+$ is orders of magnitude lower than the corresponding c_{CH}^2 term (Table 3), the frontier

orbital interaction with a base will be greater at the C–H site than at the O–H site.

In Figure 2 the experimental rate constants for C–H deprotonation of $1^+ \text{--} 5^+$ (Table 2, column 2) are reported, statistically corrected for the number of α -hydrogen atoms, against the corresponding square of the βLUMO coefficients of the benzylic C–H hydrogen atoms (c_{CH}^2) from Table 3.

The series of the 2-, 3- and 4-methoxybenzyl alcohol radical cations (empty circles) is accurately correlated by a straight line, whereas the series of the α -methyl derivatives (filled circles) shows some deviation. Overall this plot strongly suggests that proton transfer from the benzylic C–H of $1^+ \text{--} 5^+$ to water is indeed orbital controlled. A correlation analogous to that shown in Figure 2 can be obtained by plotting the log of the rate constants for C–H deprotonation against the atomic spin densities of the benzylic C–H hydrogen atoms. This is not surprising because atomic spin densities are dominated by the square of the αHOMO coefficients that in turn are similar to the βLUMO coefficients. Thus the fact that deprotonation occurs preferentially at the site bearing the largest spin density is a manifestation of the importance of frontier orbital interaction.

Calculations also show the role played by the conformation of the radical cation in determining the c_{CH}^2 value. Thus, the c_{CH}^2 decrease observed when an α -methyl group is introduced (compare 1^+ with 2^+ and 4^+ with 5^+ in Table 3), is probably due to the fact that when an α -methyl

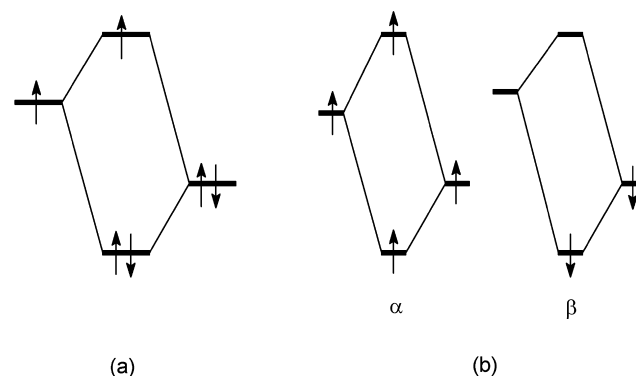


Figure 1. (a) Frontier orbital interaction of an electrophilic radical with a nucleophile by using a restricted formalism. (b) The same interaction by using an unrestricted formalism.

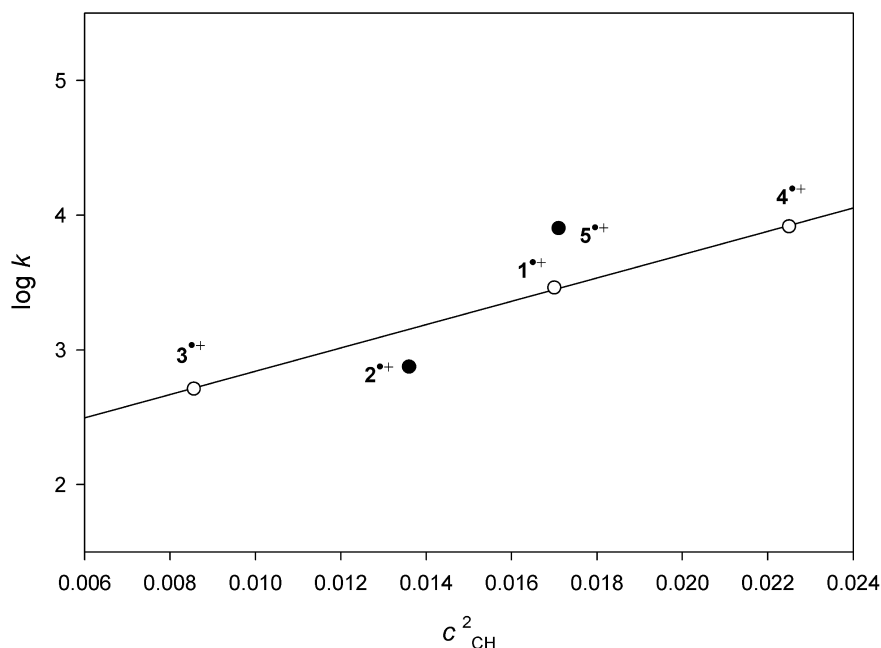


Figure 2. Correlation between the experimental rate constants for C–H deprotonation of 1^{*+} – 5^{*+} and the corresponding square of the β LUMO coefficients of the benzylic C–H hydrogen atoms (c^2_{CH}).

group is present, the most stable conformations of 2^{*+} and 5^{*+} are those in which the C_{α} – CH_3 bond is almost collinear with the aromatic π system, thus decreasing the extent of orbital overlap between the scissile C–H bond and the π system required for bond cleavage (stereoelectronic effect).^{13b,15} To this decrease in c^2_{CH} should correspond a decrease in C–H deprotonation rate on going from 1^{*+} to 2^{*+} and from 4^{*+} to 5^{*+} . However, this is observed only with the former couple, whereas 4^{*+} and 5^{*+} exhibit very similar deprotonation rates. Uncertainties in the experimental measurements could be the origin of this difference, however, it should also be considered that the stereoelectronic effect might be more marked with 2^{*+} than with 5^{*+} , due to the presence of the 2-methoxy group.

In any case, it appears clear that the stabilization of the benzylic radical formed by deprotonation of the radical cation has no significant favorable effect on the reaction rate; this confirms the hypothesis of a deprotonation reaction characterized by a very early transition state.¹³

3. Experimental

3.1. Reagents

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

2-Methoxybenzyl alcohol (**1**), 1-(2-methoxyphenyl)ethanol (**2**) and 3-methoxybenzyl alcohol (**3**) were purchased from Aldrich and purified by distillation under reduced pressure.

3.2. Reaction products

2-Methoxybenzaldehyde, 3-methoxybenzaldehyde and 2-methoxyacetophenone (Aldrich) were used as received.

3.3. Product analysis

γ -Irradiations were carried out with a panorama ^{60}Co γ -source (Nuclear Engineering) at dose rates of 0.5 Gy s^{-1} . In a typical experiment, 5 mL of an argon saturated aqueous solutions containing the substrate (2.0 mM), potassium peroxydisulfate (1.0 mM) (substrate/oxidant=2) and 2-methyl-2-propanol 0.2 M were irradiated at room temperature ($\approx 25^\circ\text{C}$) for the time necessary to obtain a 40% conversion of peroxydisulfate. Reaction products were identified and quantitatively determined by HPLC (comparison with authentic samples) using a Shimadzu LC 6A instrument equipped with a UV–Vis detector Shimadzu SPD 6A (wavelength of detection 285 nm) and a Nucleosil-5-C18 column (125 \times 4.6 mm; Macherey & Nagel). Solvent: methanol/water 1:1 (0.8 mL min^{-1}). Blank experiments were performed under every condition and showed the presence of negligible amounts of oxidation products.

3.4. Pulse radiolysis

The pulse radiolysis experiments were performed using a 3-MeV van de Graaff accelerator which supplied 300 ns pulses with doses such that 0.5 – $3 \mu\text{M}$ radicals were produced. A thermostatable continuous flow cell was employed in all experiments. The pulse radiolysis setup and the methods of data handling have been described elsewhere.¹⁶ Dosimetry was performed with N_2O saturated 10 mM KSCN aqueous solutions taking $G(\cdot\text{OH})=6.0 \times 10^{-7} \text{ mol J}^{-1}$ and $\epsilon [(\text{SCN})_2^-]=7600 \text{ M}^{-1} \text{ cm}^{-1}$ at 480 nm.¹⁷ Experiments were performed using argon saturated aqueous

solutions containing the substrate (0.1–1.0 mM), peroxydisulfate (2–10 mM) and 2-methyl-2-propanol (0.1 M). Alternatively, N₂O saturated aqueous solutions (pH ≤ 3.5) containing the substrate (0.1–0.4 mM) and thallium(I) sulfate (0.5–2.0 mM) were employed. The pH of the solutions was adjusted with NaOH or HClO₄. The temperature of the solutions was kept constant at 25 ± 0.2 °C. Rate constants were obtained by averaging 8 to 14 values, each consisting of the average of 10 to 30 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 the observed rates (*k*_{obs}) vs concentration of NaOH. For these experiments the solution containing 0.5–1.0 mM substrate, 10 mM potassium peroxydisulfate and 0.1 M 2-methyl-2-propanol was saturated with argon or oxygen and 1 mM sodium tetraborate was added to avoid undesired pH variations upon irradiation.

3.5. DFT calculations

Hybrid DFT calculations (UB3LYP) and appropriate geometry optimizations were carried out with the GAUSSIAN 98 series of programs using the 6-31G(d) basis set implemented therein.¹⁸ The calculated spin-squared expectation values (<*S*²>) were ≤ 0.762 in all cases, in good agreement with the theoretically expected value of 0.75 for a pure doublet state.

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