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The role of stereoelectronic effects on the side-chain fragmentation of alkylaromatic radical cations. The reactivity of 5-methoxy-2,2-dimethylindan-1-ol radical cation

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Abstract—A kinetic and products study of the reaction of 2,2-dimethyl-5-methoxyindan-1-ol (**1**) radical cation, in acidic aqueous solution ($pH \leq 4$) has been carried out. $\mathbf{1}^{\cdot +}$ undergoes C–H deprotonation as the exclusive reaction with $k=4.6\times10^4\ s^{-1}$. The kinetic data have been compared with those obtained for the radical cations of 1-(4-methoxyphenyl)ethanol (**2**) and 1-(4-methoxyphenyl)-2,2-dimethyl-1-propanol (**3**), suggesting that the deprotonation rate increases when the C–H bond is forced into a conformation where it is almost aligned with the π-system. The conclusion that overlap between the scissile bond and the π-system is an important requisite for the occurrence of bond cleavage is also supported by the results of DFT calculations carried out for $\mathbf{1}^{\cdot +}$ and $\mathbf{3}^{\cdot +}$. © 2002 Elsevier Science Ltd. All rights reserved.

Side-chain reactions of alkylaromatic radical cations mostly involve the cleavage of bonds between the α and β atoms, C–H and C–C bond cleavage being the most common fragmentation patterns of these reactive intermediates.[1] These reactions play a key role in synthetically useful processes[2] as well as in the chemical and enzymatic oxidative degradation of lignin and lignin model compounds to give lower molecular weight aromatic compounds.[3]

A very important aspect of the reactivity of alkylaromatic radical cations is that the rate of side-chain fragmentation can be affected by the relative orientation between the scissile bond and the aromatic π-system (*stereoelectronic effect*). As illustrated in Fig. 1, the most suitable orientation for cleavage is the one where the dihedral angle between the plane of the aromatic ring and the plane defined by the scissile bond and the atom of the aromatic ring to which this bond is connected is 90°. In this conformation the scissile bond is aligned with the π-system bearing the unpaired electron, and the best orbital overlap for bond cleavage can be achieved.[4]

The importance of stereoelectronic effects on the side-chain deprotonation of alkylaromatic radical cations has been pointed out by the studies of Tolbert and Baciocchi, dealing with 9-alkyl- and 9,10-dialkylanthracene radical cations,[5] and with alkylbenzene, 1,4-dialkylbenzene, 5,6-dimethyl- and 2,2,5,6-tetramethylindane radical cations.[6] Quantitative data have been obtained, based on the results of product studies (inter- and intramolecular selectivities).

Evidence in favor of stereoelectronic control of fragmentation in C–C bond cleavage reactions of alkylaromatic radical cations has been provided by Arnold for a variety of systems.[7,8] For example, product studies have shown that while 2,2-diphenyl-1-methoxyethane radical cation undergoes C–C bond cleavage,[9] no products deriving from this pathway but only from a reversible C–H deprotonation reaction are observed with the radical cations of the cyclic analogues 3-phenyl-2,3-dihydrobenzofuran, 5-methyl-3-phenyl-2,3-dihydrobenzofuran, *cis*- and *trans*-2-methoxy-1-phenylindane; all incorporating the β,β-diphenylethyl methyl ether moiety, where alignment between the scissile C–C bond and the π-system is prevented by the presence of the five-membered ring.[8]

Along these lines, in order to obtain more information on the role of stereoelectronic effects on the side-chain fragmentation of alkylaromatic radical cations, and in view of the lack of absolute kinetic data for these processes, we have

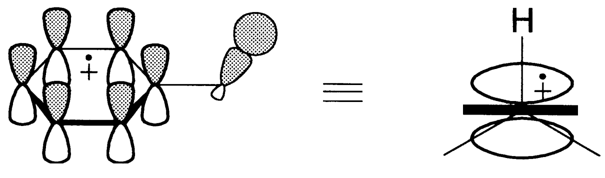

Figure 1. The most suitable orientation for C–H bond cleavage in an alkylaromatic radical cation. For the sake of clarity, in the former structure the two additional groups bonded to the benzylic carbon have been omitted. In the latter structure, the bold line represents the plane of the aromatic ring.

Keywords: stereoelectronic effect; radical cation; pulse radiolysis; deprotonation; DFT calculations.

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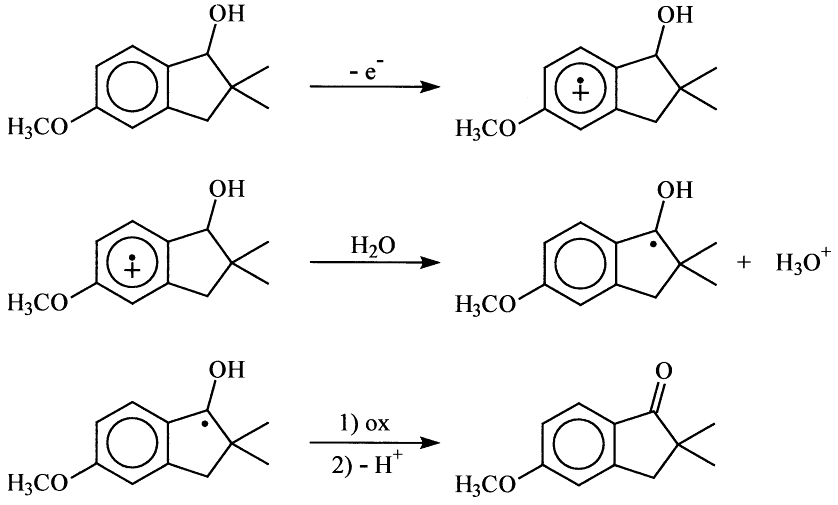
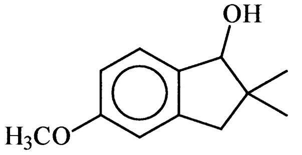


Scheme 1.

carried out a kinetic and product study of the reactivity of 2,2-dimethyl-5-methoxyindan-1-ol (**1**) radical cation, a substrate where again the presence of the five-membered ring prevents a favorable alignment between the scissile C–C bond and the π-system, favoring instead that with the C–H bond.



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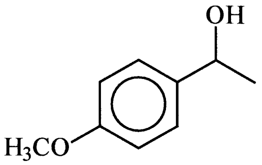

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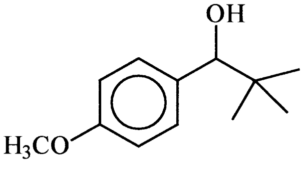

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Moreover, to provide a quantitative evaluation of these effects, the kinetic data have been compared with those obtained analogously for the radical cations of 1-(4-methoxyphenyl)ethanol (**2**) and 1-(4-methoxyphenyl)-2,2-dimethyl-1-propanol (**3**),[10] substrates structurally related to **1**, lacking however the rigidity imposed by the presence of the five-membered ring. Additional information comes from the results of DFT calculations for the determination of the equilibrium geometries of $1^{\cdot+}$ and $3^{\cdot+}$, employing the method UB3LYP/6-31G(d).

1. Results and discussion

1.1. Generation of the radical cation

$1^{\cdot+}$ was generated in aqueous solution employing either potassium 12-tungstocobalt(III)ate (from now on simply indicated as Co(III)W) or $SO_4^{\cdot-}$ as the oxidant. Co(III)W is a well-known one-electron chemical oxidant able to oxidize methoxybenzene derivatives via outer-sphere electron transfer.[11–13] $SO_4^{\cdot-}$ is a strong oxidant which is able to react with aromatic substrates via electron transfer to yield the corresponding radical cations with $k \approx 10^9\ M^{-1}\ s^{-1}$ (Eq. (1)).[14–16]

$$SO_4^{\cdot-} + ArCH(X)R \rightarrow SO_4^{2-} + Ar^{\cdot+}\ CH(X)R \tag{1}$$

$SO_4^{\cdot-}$ has been generated either photochemically by steady-state irradiation (λ=254 nm) of aqueous $K_2S_2O_8$ solutions (Eq. (2));

$$S_2O_8^{2-} \underset{254\ nm}{\overset{h\nu}{\rightarrow}} 2SO_4^{\cdot-} \tag{2}$$

or by chemical radiation (pulse and steady-state γ-radiolysis) according to Eqs. (3)–(5).

$$H_2O \rightsquigarrow H^+, \cdot OH, e_{aq}^- \tag{3}$$

$$\cdot OH + CH_3C(CH_3)_2OH \rightarrow H_2O + \dot{C}H_2C(CH_3)_2OH \tag{4}$$

$$e_{aq}^- + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{\cdot-} \tag{5}$$

Radiolysis of water leads to the formation of the hydroxyl radical (·OH) and the hydrated electron (e_{aq}^-) (Eq. (3)). The former is scavenged by 2-methyl-2-propanol (Eq. (4); $k=6\times10^8\ M^{-1}\ s^{-1}$),[14] while e_{aq}^- reacts with the peroxydisulfate anion leading to the formation of $SO_4^{\cdot-}$ (Eq. (5); $k=1.2\times10^{10}\ M^{-1}\ s^{-1}$).[14]

1.2. Product studies

The oxidation of **1** was carried out at pH 3.1 employing Co(III)W or $SO_4^{\cdot-}$ as the oxidant, showing in all cases the exclusive formation of 5-methoxy-2,2-dimethylindan-1-one.

Ketone formation can be readily explained on the basis of the formation and deprotonation of an intermediate radical cation leading to a 1-hydroxyindanyl radical, which is then oxidized to give 5-methoxy-2,2-dimethylindan-1-one (Scheme 1), in analogy with one-electron oxidations of

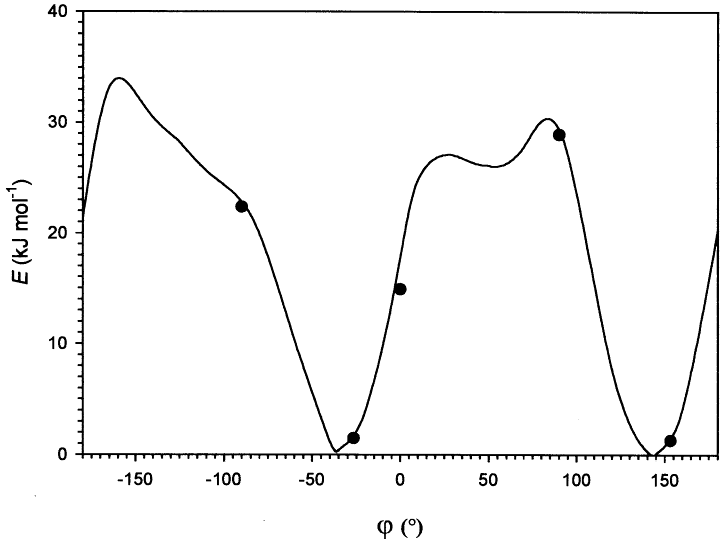


Figure 2. Adiabatic potential energy curve for the internal rotation about the benzylic bond of $3^{\bullet +}$ calculated by the UB3LYP/6-31G(d) method. The dihedral angle φ is measured between the benzylic C–H bond and the aromatic ring plane. The points refer to the Newman projection formulae shown in Scheme 2.

arylalkanols.[17] Thus, the exclusive reaction of $1^{\bullet +}$ is deprotonation from C-1.

1.3. Kinetic studies

These were carried out using the pulse radiolysis technique. The time-resolved absorption spectra of $1^{\bullet +}$ at pH 3.5 and room temperature show the characteristic UV and visible absorption bands of anisole-type radical cations centered at 290 and 460 nm.[10,15,18] The decay rate of the radical cation was measured spectrophotometrically following the decrease in optical density at 460 nm. Under these conditions, $1^{\bullet +}$ decays with first-order kinetics with $k=4.6\times10^4\ \mathrm{s}^{-1}$, in a reaction which, on the basis of product analysis results, is assigned to C–H deprotonation.

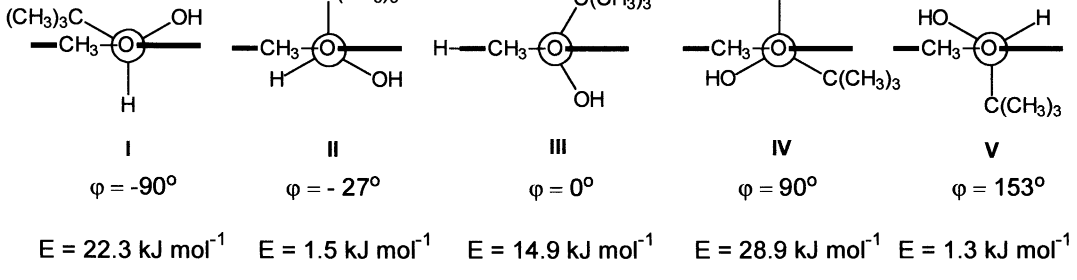
The rate constant for deprotonation from $1^{\bullet +}$, $k=4.6\times10^4\ \mathrm{s}^{-1}$, can be compared with that measured under analogous conditions for $2^{\bullet +}$, which also undergoes exclusive deprotonation with $k=7.0\times10^3\ \mathrm{s}^{-1}$.[10] These results indicate that when the C–H bond is forced into a conformation where it is almost aligned with the π-system as in $1^{\bullet +}$, the deprotonation rate increases significantly (ca. 6.5 times) as compared to $2^{\bullet +}$, where all conformations are instead accessible for the scissile C–H bond.[19]

It is also very interesting to compare the reactivity of $1^{\bullet +}$ with that of $3^{\bullet +}$ which undergoes exclusive C–C bond cleavage with $k=1.5\times10^5\ \mathrm{s}^{-1}$.[10] This behavior is attributed to a stereoelectronic effect since the presence of the bulky *tert*-butyl group disfavors the most suitable conformation for C–H bond cleavage, where the scissile C–H bond is aligned with the π-system due to its interaction with the *ortho*-hydrogens. Unfortunately, because the radical cations $1^{\bullet +}$ and $3^{\bullet +}$ are relative short lived intermediates, this hypothesis cannot be easily confirmed by direct observation (ESR) of the radical cations. It is however nicely supported by the results of DFT calculations.

The adiabatic potential energy curve for the rotation about the benzylic bond of $3^{\bullet +}$ has been calculated by the UB3LYP/6-31G(d) method with a resolution of 20° (Fig. 2). It shows that the two conformations where the scissile C–H bond is aligned with the π-system (Scheme 2, conformations **I** and **IV**) are characterized by significantly higher energies (≈21–27 kJ mol^{-1}) than those most suitable for C–C bond cleavage (conformations **II** and **V**) where is the C–C(CH$_3$)$_3$ bond to be aligned with the π-system.

In particular, conformations **II** and **V** are very close in energy to the two minima at $\varphi=-34°$ and 144.5°, respectively.

With $1^{\bullet +}$, the results of DFT calculations show that the most stable structure is that in which the scissile C–H bond is almost aligned with the π-system (*pseudo axial*),



Scheme 2.

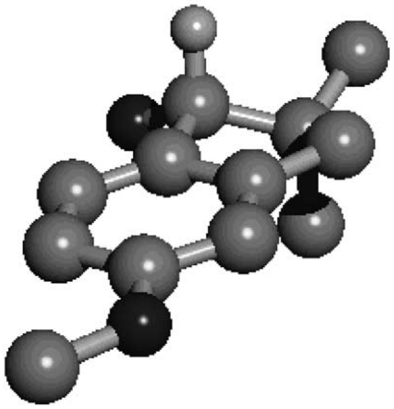


Figure 3. Most stable conformation for **1**$^{\cdot+}$, optimized by the UB3LYP/6-31G(d) method. All hydrogen atoms except the benzylic one bonded to C-1 have been omitted for clarity.

characterized by a dihedral angle between the benzylic C–H bond and the aromatic ring plane of $\varphi=92.4°$ (Fig. 3).

A conformation where the C–C bond is aligned with the π-system is impossible to reach in this case because of the very high strain energy involved, and accordingly deprotonation is the exclusive reaction pathway for **1**$^{\cdot+}$. By assuming that the amount of products deriving from C–H bond cleavage in **3**$^{\cdot+}$ is $\leq 0.5\%$,[10,18] it is possible to set an upper limit for the deprotonation rate as $k \leq 7.5\times10^{2}\ \mathrm{s}^{-1}$, a value which indicates that the deprotonation rate increases at least 60 times on going from **3**$^{\cdot+}$ to **1**$^{\cdot+}$.

In conclusion, this work provides evidence for the importance of stereoelectronic effects in the deprotonation of alkylaromatic radical cations, in full agreement with the studies of Tolbert[5] and Baciocchi.[6] In the radical cations of indan-1-ol derivatives, an increase in deprotonation rate results from the alignment between the scissile C–H bond and the π-system imposed by the presence of the five-membered ring. The absolute rate constant for deprotonation of **1**$^{\cdot+}$ has been measured, providing a quantitative evaluation of this effect. In contrast, C–C bond cleavage appears to be strongly depressed in these systems, as shown by the comparison between two structurally related radical cations **1**$^{\cdot+}$ and **3**$^{\cdot+}$, undergoing exclusive C–H and C–C bond cleavage, respectively. This result clearly indicates that in alkylaromatic radical cations, overlap between the scissile bond and the π-system containing the unpaired electron is an important requisite for the occurrence of bond cleavage, a result which is nicely supported by DFT calculations carried out for **1**$^{\cdot+}$ and **3**$^{\cdot+}$.

However, Gilbert pointed out that there could be exceptions to this behavior when specific structural features favor C–C bond cleavage without stereoelectronic assistance. Accordingly, 2-indanol radical cation undergoes C–C bond cleavage yielding the 2-(2-oxoethyl)benzyl radical,[21] a result which has been explained in terms of the loss of ring strain resulting from ring-opening and the stability of the radical and cation fragments formed.

An alternative explanation able to account for this behavior might also be that under the experimental conditions employed by Gilbert, the 2-indanol radical cation undergoes α-OH deprotonation, followed by C–C bond cleavage in an intermediate 2-indanyloxyl radical and/or 2-indanol radical zwitterion (Scheme 3), as described for 1-(4-methoxyphenyl)-2-alkanol radical cations.[22,23]

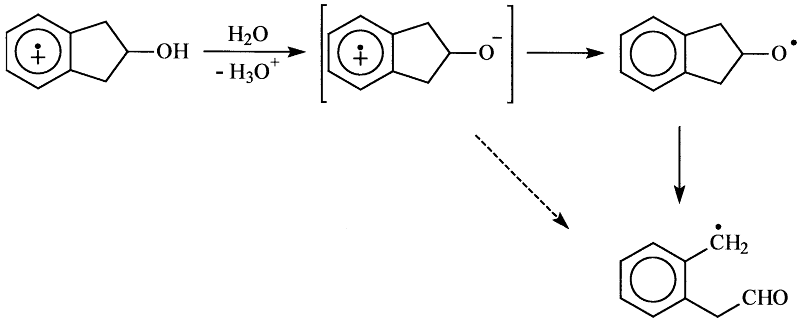
2. Experimental

2.1. Reagents

Potassium peroxydisulfate, perchloric acid and 2-methyl-2-propanol were of the highest commercial quality available. Milli-Q-filtered (Millipore) water was used for all solutions. Potassium 12-tungstocobalt(III)ate was prepared as described previously.[13]

2,2-Dimethyl-5-methoxyindan-1-ol (**1**) was prepared by reduction of 2,2-dimethyl-5-methoxyindan-1-one with $\mathrm{NaBH_4}$ in 2-propanol. ^{1}H NMR ($\mathrm{CDCl_3}$), δ (ppm): 7.29–6.73 (m, 3H, Ar*H*); 4.60 (s, 1H, ArC*H*OH); 3.79 (s, 3H, OCH_3); 2.81–2.56 (m, 2H, CH_2); 1.14 (s, 3H, CH_3); 1.06 (s, 3H, CH_3).[24]

2,2-Dimethyl-5-methoxyindan-1-one was prepared by reaction of 5-methoxyindan-1-one with sodium hydride and excess methyl iodide in anhydrous tetrahydrofuran. ^{1}H NMR ($\mathrm{CDCl_3}$), δ (ppm): 7.71–6.86 (m, 3H, Ar*H*); 3.88 (s, 3H, OCH_3); 2.95 (s, 2H, CH_2); 1.22 (s, 6H, CH_3). ^{13}C NMR ($\mathrm{CDCl_3}$), δ (ppm): 209.68 (CO); 165.44 (Ar C-6); 155.14 (Ar C-9); 128.45 (Ar C-5); 126.07 (Ar C-4); 115.38 (Ar C-7); 109.7 (Ar C-8); 55.6 ($\mathrm{OCH_3}$); 45.62 (C-2); 42.91 ($\mathrm{2CH_3}$); 25.38 (C-3).[24]



Scheme 3.

2.2. Product analysis

All reactions were carried out in a 50 mM citrate buffer solution (pH 3.1). Reaction products were identified and quantitatively determined by GC (comparison with authentic samples) and GC–MS analysis. In order to check the stability of the substrates to reaction conditions, blank experiments were performed under every condition showing, in the reactions with $K_2S_2O_8$, the presence of negligible amounts of oxidation products.

Oxidations induced by Co(III)W were performed at T=50°C. In a typical experiment, 5 mL of an argon-saturated solution containing the substrate (1–2 mM) and Co(III)W (1–2 mM) were stirred until complete conversion of the oxidant. Workup was performed as described previously.[12]

Steady-state photolysis was carried out employing a Photochemical Multirays Reactor (Helios Italquartz) equipped with 10×15 W 254 nm lamps. Five milliliters of an argon-saturated solution containing **1** (2 mM) and $K_2S_2O_8$ (0.1 M) was irradiated at room temperature for 1 min showing quantitative conversion of **1** in 2,2-dimethyl-5-methoxyindan-1-one.

Steady-state γ-radiolysis was carried out with a ^{60}Co γ-source (source activity: ≈0.5 Mrad/h). Five milliliters of a nitrogen-saturated aqueous solutions containing **1** (1 mM), $K_2S_2O_8$ (0.1 mM) and 2-methyl-2-propanol (0.2 M) was irradiated at room temperature for 18 min showing the formation of 2,2-dimethyl-5-methoxyindan-1-one as the exclusive oxidation product.

2.3. Pulse radiolysis

The pulse radiolysis experiments were performed using a Varian linear accelerator providing 5 MeV electron pulses of duration ≤200 ns with doses such that 1–3 μM radicals were produced. A continuous flow cell was employed in all experiments. The pulse radiolysis setup and the methods of data handling have been described elsewhere.[25] Experiments were performed at room temperature, using argon- or oxygen-saturated aqueous solutions containing the substrate (0.1–0.25 mM), peroxydisulfate (5 mM) and 2-methyl-2-propanol (0.1 M). The pH of the solutions was adjusted with $HClO_4$. Rate constants were obtained by averaging at least three values, each consisting of the average of 8–16 shots.

2.4. 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.[26] This method was used because the results it provides for cation radicals have been found to be very reliable.[27] The calculated spin-squared expectation values ($\langle S^2 \rangle$) were ≤0.762 in all cases, in good agreement with the theoretically expected value of 0.75 for a pure doublet state. The relaxed potential energy surface scan for the internal rotation about the benzylic bond of $\mathbf{3}^{\cdot +}$ was carried out in redundant internal coordinates in steps of 20°. The energy results reported in Fig. 2 are relative to the global minimum structure corresponding to φ=144.5°. The calculations relative to $\mathbf{1}^{\cdot +}$ indicated the conformation with the benzylic hydrogen in pseudo axial position (φ=92.4°) as the most stable (Fig. 3), whereas that with the benzylic hydrogen in pseudo-equatorial position (φ=45.7°) resulted to be 3.5 kcal mol^{-1} higher in energy.

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