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Photo- and radiation-chemical production of radical cations of methylbenzenes and benzyl alcohols and their reactivity in aqueous solution

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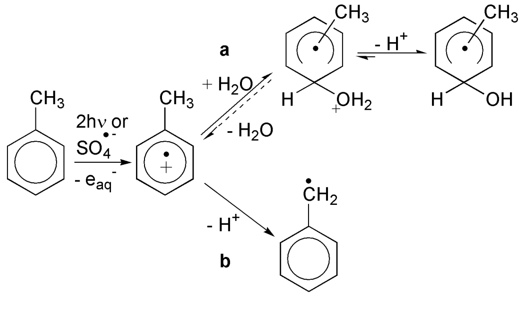
Radical cations of methylated benzenes and benzyl alcohols were generated by photoionization and by reaction with the oxidant $SO_4^{\bullet -}$ in aqueous solution. The photoionization requires two 248 nm photons. The lifetimes and absorption spectra of the radical cations produced were determined by time-resolved conductance and optical detection, and the reaction products were measured by GC. As expected, the radical cation lifetimes increase strongly with increasing number of additional methyl groups, and so does the ratio of deprotonation from a methyl or hydroxymethyl group *vs.* addition (of water) to a ring position. In the case of toluene the radical cation appears to have a chemical lifetime τ of 10–100 ps $\leq \tau \leq$ 20 ns, *i.e.*, longer than it takes for an ion pair to separate into the free (solvated) ions, and it reacts predominantly by addition of water to the ring rather than by deprotonation from the methyl group. A further observation is that, as compared to *methoxylated* analogues, the methylated benzyl alcohol radical cations are much more reactive, such that OH^--induction of side-chain fragmentation, as often required with methoxylated benzyl alcohol-type radical cations, is not necessary.

Introduction

Whereas information is available on radical cations of alkylbenzenes either neat or dissolved in *organic* solvents or low-temperature glasses,[1–3] rather little is known[4–8] about the nature and reactivities of these species in *aqueous* solution. The study of these molecules in water is, of course, difficult due to their low solubility but it is of interest because it is possible that in water specific *ionic* reactions may occur. These may be of *practical* interest in connection with the removal of aromatic impurities in drinking water by photochemical means.

It is probable that in polar solvents the radical cations decay very rapidly (due to the typical unimolecular decay reactions of radical cations such as side chain deprotonation (Scheme 1 (b) or C–C-fragmentation, Scheme 3 below).[9] If the solvent is a nucleophilic one such as water, addition to the ring yielding a hydroxycyclohexadienyl radical and H^+ (Scheme 1 path (a))[10] will further decrease the lifetime, *e.g.*, in the case of toluene, see Scheme 1.

The aim of this laser flash photolysis study is to rapidly generate methylated *benzene* and ring-methylated *benzyl alcohol* (as representatives of simple, non-stabilized aromatics) radical cations in aqueous solution, to determine their lifetimes and characteristic reactions and to identify (some of) their products.



Scheme 1

Results and discussion

1. Methylbenzenes ArCH$_3$

1.1 Time-resolved experiments*Direct photoionization.* The 248 nm laser photolysis (20 ns pulse duration) of methylbenzenes in aqueous solution in all cases led to the production of the hydrated electron, e_{aq}^-, as concluded from its characteristic[11] absorption spectrum with a maximum at ≈700 nm (for an example, see Fig. 1) and by its reactivity[12] with electron scavengers such as O_2, N_2O or alkyl chlorides. The production of the electron, which turned out to require *two* photons (*bi*photonic reaction, see Fig. 2) means that a radical cation is also formed. As shown in the following, radical cations could in fact be directly observed, but only in the cases of *multiply* methylated benzenes. For *toluene*, the radical cation turned out to be too short-lived (lifetime < 20 ns). For this reason, product analysis studies were also performed (with the hope of detecting the radical cation *via* its reaction products (see section 1.2)).

The time-resolved absorption spectra recorded on direct 248 nm photolysis of *p*-xylene (≡*p*-Xy) in deoxygenated aqueous solution are shown in Fig. 1. At 0.3 µs after the pulse there is a strong peak at 268 nm, shoulders at 290 and 440 nm and a very strong and broad band with a maximum at ≈720 nm.

The broad band is due to the hydrated electron, e_{aq}^-, as shown by its reactivity with the electron traps 2-chloroethanol, dichloromethane, O_2 or N_2O. The presence of e_{aq}^- proves that ionization has occurred. It is concluded that the radical cation so formed is responsible for the absorption at 290 nm, while the strong peak centered at 268 nm and the shoulder at 320

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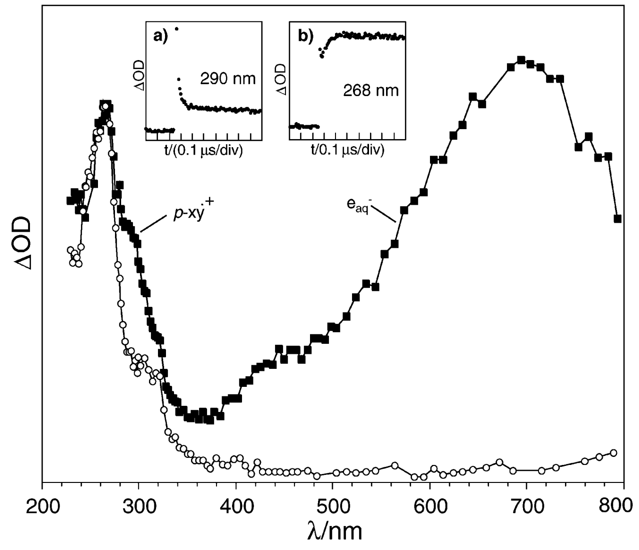


Fig. 1 Absorption spectra observed on 248 nm photolysis (70 mJ per pulse) of *p*-xylene (2 mM) in Ar-saturated H_2O 0.3 μs (■) after the pulse. The spectrum observed 3 μs after the pulse (○) was recorded in the presence of 0.15 M 2-chloroethanol as an e_{aq}^- scavenger. In inset (a) is shown the decay of the radical cation, in inset (b) the concomitant formation of the 4-methylbenzyl radical.

nm are attributed to the 4-methylbenzyl radical, which is formed from the radical cation by deprotonation from a methyl group. At 3 μs after the pulse the radical cation absorption at 290 nm and the e_{aq}^- have decayed leaving a "clean" spectrum of the 4-methylbenzyl radical (see Fig. 1), characterized by one strong absorption at 268 nm and two weaker peaks at 310 and 322 nm.

To obtain information about the *mechanism* of 248 nm photoionization of methylbenzenes in aqueous solution, the dependence of the yield of e_{aq}^- on the laser intensity was investigated by attenuating the laser light with neutral density filters. Fig. 2 shows the situation for toluene, used as a model.

As is evident, the yield of e_{aq}^-, monitored *via* its absorbance at 650 nm, increases quadratically with the energy per pulse, indicating that the process is biphotonic, *i.e.*, a first-formed excited state (eqn. (1)) is ionized by interaction with a second photon (eqn. (2)):

$$\mathrm{ArCH_3} \xrightarrow{h\nu(248\,\mathrm{nm})} \mathrm{ArCH_3}^* \tag{1}$$

$$\mathrm{ArCH_3}^* \xrightarrow{h\nu(248\,\mathrm{nm})} \mathrm{ArCH_3}^{\bullet+} + \mathrm{e_{aq}}- \tag{2}$$

This result is in line with what is expected on the basis of the gas-phase ionization potential, IP, of the substrate studied. For example, the IP of toluene is 8.8 eV while the energy associated with a 248 nm photon (5 eV) plus the free energy of hydration of an organic cation and of the electron (3–3.5 eV)[13] add up to only 8–8.5 eV. A monophotonic ionization is therefore thermodynamically not possible. On the other hand, *p*-xylene, whose IP is 8.44 V, is a limiting case, its monophotonic photoionization *could* be thermodynamically feasible. It turned out, however, that the ionization is *bi*photonic.

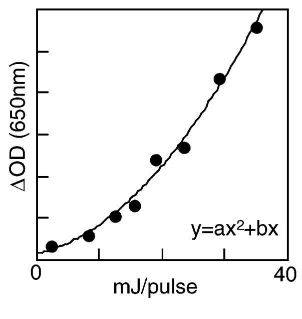


Fig. 2 Dependence of the absorbance (optical density) due to the hydrated electron (monitored at 650 nm) on the laser power following 248-nm flash photolysis of a deoxygenated aqueous solution of toluene (saturated).

To obtain information about the *lifetimes* (*via* the rates of decay) of methylbenzene radical cations in aqueous solution, photolysis experiments with time-resolved *conductance* detection were carried out. As seen from Fig. 3(a)–(c), on photolysis in acidic solution there is, after the pulse, a first-order increase of conductance which is explained in terms of replacement of $Ar^{\bullet+}$–CH_3 (produced in the photoionization) by the much more mobile H^+ ion produced by deprotonation from –CH_3 or by nucleophilic addition of water (see Scheme 1, steps (a) and (b)). In basic solution, after the pulse, the conductance *de*creases (Fig. 3(d)) since the proton formed is neutralized by the OH^- ion whose concentration is thereby reduced. This "neutralization" proves that the positive ion produced on interaction with water is the proton.

As mentioned, the conductance *increase* traces were exponential and the rate constants measured were the same, independent of the method of production (photoionization or reaction with $SO_4^{\bullet-}$, see below) as those measured optically for the *decay* of the radical cations at their λ_{max} values (this was possible only for the long-lived radical cations). The deprotonation rates thus obtained for several methylbenzenes are collected in Table 1.

As seen from the data in Table 1, for benzene, toluene, *m*-xylene and 1,3,5-trimethylbenzene the lifetime of the radical cation is shorter than the laser pulse width of 20 ns,[15] *i.e.*, the rate constant for their decay is $\geq 5 \times 10^7\ s^{-1}$. The rate constant for the decay reaction in aqueous solution decreases by more than three orders of magnitude as the number of methyl groups goes from one to four. As the electron density increases in this direction (as concluded from the decrease of ionization potential)[16] an increase in the stability of the radical cation and a change[17] in the reaction path are observed (see section 1.2). In the case of benzene, whose radical cation has no side-chain from which to deprotonate, addition of water occurs to produce the hydroxycyclohexadienyl radical ("OH adduct"), which, under oxidizing conditions, leads to phenol as the non-radical, final product.[18]

Column 4 of Table 1 contains a collection of rate constants determined previously by *pulse radiolysis*. In these cases the radical cations were produced from the OH-adducts (formed

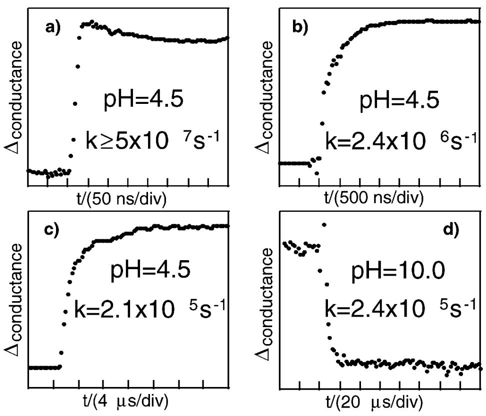


Fig. 3 Photolysis-induced change of conductance of deoxygenated aqueous solutions at pH = 4.5 of: (a) 5 mM toluene, (b) 2 mM p-xylene and (c) 1 mM 1,2,4-trimethylbenzene, containing 1.2% of 2-chloroethanol to scavenge e^-_{aq}. For 1,2,4-trimethylbenzene the change of conductance at pH = 10 is also shown (d).

Table 1 Rate constants (s^{-1})[a] for decay of methylbenzene radical cations in aqueous solution

Aromatic	Conductance detection[b c]	Optical detection[c]	From refs. 4, 5 (optical detection)
Benzene	$\geq 5 \times 10^7$		
Toluene	$\geq 5 \times 10^7$		1.0×10^7
o-Xylene	2×10^7		2.0×10^6
m-Xylene	$\geq 5 \times 10^7$		2.0×10^6
p-Xylene	2.4×10^6	1.8×10^6	1.4×10^6
(*p*-Methoxytoluene)	4.0×10^2[d]		
1,3,5-Trimethylbenzene	$\geq 5 \times 10^7$		1.5×10^6
1,2,3-Trimethylbenzene	4×10^6		1.5×10^6
1,2,4-Trimethylbenzene	3×10^5	2.8×10^5	2.0×10^5
1,2,4,5-Tetramethylbenzene	$4.4. \times 10^4$[e]	4.1×10^4[e f]	2.7×10^4

[a] Accuracy: ±10%. [b] At pH = 4.5. [c] This work. [d] From ref. 14 [e] In water/acetonitrile 3 : 1, for solubility reasons. [f] Obtained by monitoring the decay of the radical cation (formed by reaction with $SO_4^{\bullet-}$) at its $\lambda_{\max}$.

by addition of $^{\bullet}OH$ to the methylbenzenes) by H^+-induced dehydration (analogous to the *reverse* of reaction (a) in Scheme 1), *i.e.*, by two *bi*molecular reactions, whereby the rate of the first one (addition of $^{\bullet}OH$) depends on [methylbenzene], typically a very low value even in saturated aqueous solution. Thus, with the less long-lived radical cations, their *formation* is likely to be rate-determining (unlike the photoionization method where radical cation formation occurs in ≤20 ns). In the latter cases, the rate constant for decay of the radical cations will be *underestimated*, and this is probably the reason why many of the values given by Sehested *et al.*[4,5] are smaller (often by more than of factor of 10, see Table 1) than the values measured by us.

As concluded from the product analysis data (see section 1.2), in the case of toluene, addition of water is still the most important reaction of the radical cation, but deprotonation from the methyl group (see Scheme 1, path (b)) also takes place (6%). In strongly acidic solution ($[H^+] \geq 1$ M), protonation of the OH-adduct makes the hydration reaction partly reversible; since the deprotonation from the methyl group is an irreversible reaction, under these conditions the dominant final (transient) product is the benzyl radical.

Oxidation with $SO_4^{\bullet-}$. Due to its highly positive reduction potential,[19,20] the $SO_4^{\bullet-}$ radical is a potent one-electron oxidant, particularly with respect to aromatic compounds.[21–24] Aqueous solutions containing potassium peroxydisulfate and the substrates were photolyzed with 20 ns pulses of 248 nm light. The concentrations were chosen such that the main part of the light was absorbed by $S_2O_8^{2-}$, which homolyzes to yield two $SO_4^{\bullet-}$ radicals (eqn. (3)). The $SO_4^{\bullet-}$ radical then reacts with the aromatic compound by electron transfer (eqn. (4)) yielding the corresponding radical cation.

$$S_2O_8^{2-} \xrightarrow{h\nu(248\,\mathrm{nm})} 2SO_4^{\bullet-} \qquad (3)$$

$$SO_4^{\bullet-} + \mathrm{Ar} \longrightarrow \mathrm{Ar}^{\bullet+} + SO_4^{2-} \qquad (4)$$

For *p*-xylene, the resulting time-resolved absorption spectra are shown in Fig. 4.

At 50 ns after the pulse, there is negative ΔOD at $\lambda < 290$ nm (due to the depletion of $S_2O_8^{2-}$ and, to a lesser extent, of *p*-Xy) and a broad band (positive ΔOD) centered at 450 nm, due to $SO_4^{\bullet-}$ (eqn. (3)). The (weak) negative signal in the region 550 to 750 nm is assigned to luminescence emission. After 170 ns the intensity of the band at 450 nm has grown and during this time there has developed a strong band with $\lambda_{\max}$ 290 nm; this is explained in terms of the formation of the radical cation *p*-$\mathrm{Xy}^{\bullet+}$ *via* eqn. (4), this assignment being in good agreement with the characterization of the *p*-Xy radical cation by Sehested *et al.*[4,5] using the pulse-radiolysis technique. The shoulder at 350 nm (which can be scavenged by O_2) is tentatively assigned[25] to triplet *p*-Xy formed by the small portion of light (≈9%) absorbed by *p*-Xy directly.

After 35 μs both radical cation absorptions have decayed and are replaced by a new spectrum characterized by 4 peaks, a strong one with $\lambda_{\max}$ 268, and three less intense peaks at 298, 310 and 322 nm. These are attributed to the 4-methylbenzylradical, formed by rapid deprotonation of the radical cation (eqn. (5)):

$$\mathrm{ArCH_3}^{\bullet+} \longrightarrow \mathrm{ArCH_2}^{\bullet} + H^+ \qquad (5)$$

To support this assignment, the *p*-methylbenzyl radical was generated independently by H atom abstraction from *p*-Xy by the radiation-chemically produced $O^{\bullet-}$.[26] It showed an identical spectrum both at 268 nm and in the 290–320 nm "fingerprint region".[27] The effect of the introduction of oxygen into the solution confirms these assignments: In the presence of oxygen the benzyl radical bands decayed rapidly, whereas the radical cation bands ($\lambda_{\max}$ 290, 435 nm) were essentially unaffected.

It was attempted to determine the bimolecular rate constants for reaction of methyl-substituted benzenes with $SO_4^{\bullet-}$ by

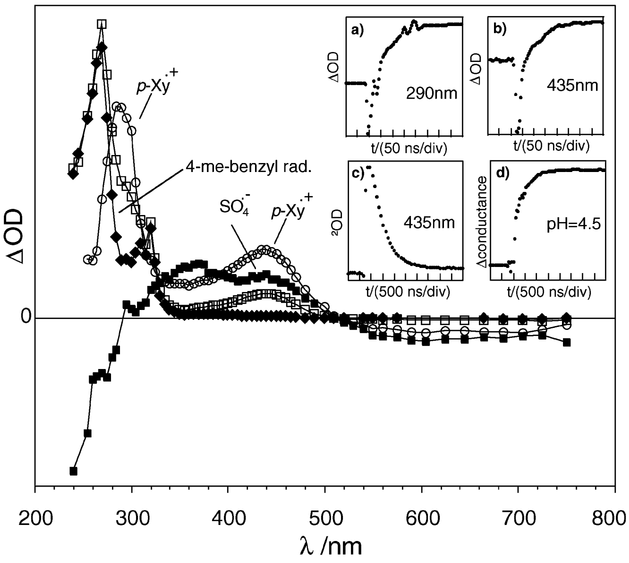


Fig. 4 Absorption spectra recorded on 248 nm photolysis of 70 mM $K_2S_2O_8$ in the presence of 2 mM *p*-xylene in Ar-saturated H_2O, pH = 3.6: 50 ns (■), 175 ns (○), 1 μs (□), 35 μs (◆) after the pulse. Insets (a) and (b) show the build up of the radical cation at 290 nm and 435 nm. In inset (c) is shown the decay of the radical cation at 435 nm. In inset (d) is shown the conductance increase induced by direct photolysis of 2 mM *p*-Xy at pH = 4.5 by which $\mathrm{Xy}^{\bullet+}$ is formed whose decay leads to H^+ (eqn. (5)).

Table 2 Products from one-electron oxidation of toluene

Conditions[a]	Products (10^{-7} M)					
	Cresols (*o* : *m* : *p*)	Benzylalcohol	Bibenzyl	Other products	% addition	% deprotonation
LFP (248) in H_2O + $K_3Fe(CN)_6$[b c]	5.8 (42:8:50)	0.4	0.01	Photoadducts[d]	94	6
LFP (248) in H_2O[b], no additive	3.8 (37:8:55)	0.5	0.04	Photoadducts[d]	87	13
LFP (248) in CH_3CN [b]	—	0.2	0.6	PhCHO $PhCH_2CH_2CN$	—	100
($SO_4^{\bullet-}$ + $K_3Fe(CN)_6$) (γ-radiolysis)[e]	9.7 (43:7:50)	0.2	—	PhCHO (0.4)	94	6

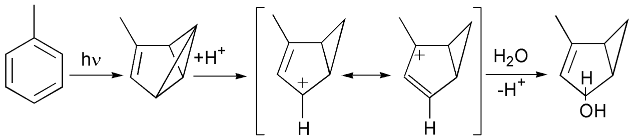
[a] In all experiments a saturated solution of toluene (6 mM) was degassed with toluene-saturated Ar. [b] Solutions were irradiated with 1000 pulses (20 ns, ≈150 mJ per pulse) of 248 nm laser light. [c] The concentration of the ferricyanide added was 0.25 mM; this value was chosen to ensure that the absorbance of the substrate at 248 nm (OD(Tol)/cm = 0.4) is higher than that of the oxidant ($OD(Fe(CN)_6^{3-}) = 0.2$). [d] These products were also obtained from (steady state) irradiation with a medium pressure Hg lamp. [e] In the presence of 2 mM $K_2S_2O_8$ (to scavenge e_{aq}^-), 1 M t-BuOH (to scavenge $^\bullet$OH) and 5 mM $K_3Fe(CN)_6$ (to scavenge the OH-adducts), Ar-saturated solution pH = 4.3.

measuring k_{obs}, the rate of the optical density increase of the radical cation, as a function of the concentration of added substrate. However, only for the case of durene was the lifetime of the radical cation long enough ($\tau = 23$ μs) to observe its complete build-up. In this case the bimolecular rate constant for reaction with $SO_4^{\bullet-}$ (determined from the slope of the linear plot of k_{obs} *vs.* [durene]) is 4.6×10^9 M^{-1} s^{-1}.

1.2 Product analysis results. To substantiate the mechanistic conclusions drawn from the time-resolved experiments, an attempt was made to identify the most important non-radical products from the reactions of the radical cations, taking toluene and *p*-xylene as examples. Saturated solutions of toluene (OD/cm ≈ 0.4 at 248 nm) were photolyzed with 150–200 mJ pulses of 248 nm laser light. The solutions contained $K_3Fe(CN)_6$ as a mild oxidant in order to convert any photogenerated hydroxycyclohexadienyl radicals into the corresponding phenols.[18,28] The results are presented in Table 2.

As can be seen from the data in Table 2, the major products found are the isomers of cresol (> 90% of the total photoionization products). These are suggested to be formed from the radical cation *via* addition of water to the ring followed by oxidation of the isomeric hydroxycyclohexadienyl radicals (OH adducts) by $K_3Fe(CN)_6$ (Scheme 2, path (a)).[29] Small amounts of benzyl alcohol, traces of bibenzyl and of benzaldehyde were also found. These are suggested to derive from side-chain deprotonation of the radical cation (path (b)) followed by oxidation of the resulting benzyl radical[30] and addition of water to the (incipient) benzyl cation. On this basis, benzaldehyde is a secondary product, originating from benzyl alcohol. A particularly interesting piece of information is that the isomer distribution of the cresols formed is independent of the way of generation of the toluene radical cation (biphotonic ionization *vs.* oxidation by $SO_4^{\bullet-}$). This is in contrast to the situation with benzyl alcohol, where the distribution of the hydroxymethylphenols formed from the radical cation clearly depends on its method of production.[10] The latter phenomenon was explained in terms of the different nature (and therefore lifetime) of the reacting species, *i.e.*, ion *pair* formation in the case of the reaction with $SO_4^{\bullet-}$ and formation of the "naked" radical cation in the case of photoionization. The difference in the behavior of benzyl alcohol and toluene can then be understood by assuming that the radical cation of toluene is less reactive than that of benzyl alcohol such that the former undergoes nucleophilic addition of water when it is in the fully hydrated state and not already when it is in the (earlier) ion *pair* state (see also below). Since solvation times of organic ions in water appear to be typically in the 10 to 25 ps range, (ref. 31 and references therein) the chemical lifetime of the toluene radical cation must be ≥ this value.

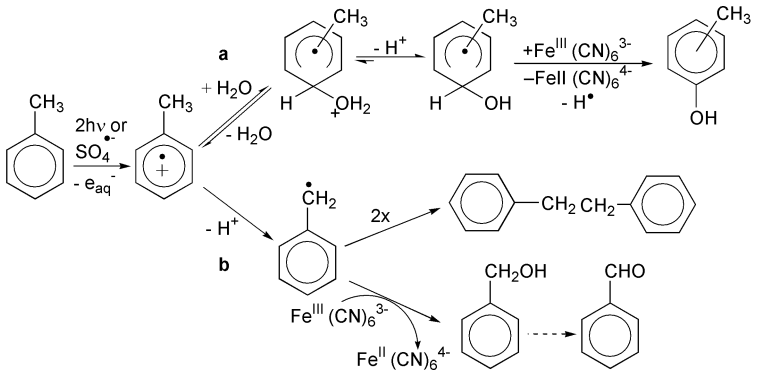
In the 248 nm laser photolysis experiments, additional products were found which were also produced on photolysis of toluene with the *low*-intensity light (254 nm) of a medium-pressure mercury lamp. On the basis of their mass spectra,[32] the products are identified as isomers of the photoadduct of water to electronically excited toluene, *e.g.*, eqn. (6).[33]



(6)

In line with this suggestion, these products were not found on photolysis of toluene in pure CH_3CN or on generating the radical cation by reaction with the radiation-chemically produced $SO_4^{\bullet-}$ (see below).

To additionally test the ideas contained in Schemes 1 and 2, the toluene radical cation was produced in a *non*-photochemical way, *i.e.* by reaction with *radiation*-chemically produced



Scheme 2

Table 3 Products from 248 nm photolysis of aqueous solutions of *p*-xylene

	Products, (10^{-7} M)					
Conditions[a]	2,5-Dimethyl phenol	4-Methyl benzylalcohol	Di-(*p*-tolyl) Ethane	Other products	% Addition	% Deprotonation
LFP (248) in $H_2O + K_3Fe(CN)_6$[b]	1.6	1.5	0.2	4-Methylbenzaldehyde (0.09) Dimer (0.03)	44	56
LFP (248) in H_2O	1.2	0.4	3.5	4-Methylbenzaldehyde (0.02)	14	86
LFP (248) in CH_3CN	—	0.2	1.0	4-Methylbenzaldehyde (0.05) Dimer (0.8)	—	100

[a] In all experiments saturated solutions of *p*-Xy (2 mM) were degassed with *p*-Xy-saturated Ar and irradiated with 1000 pulses (20 ns, 150 mJ per pulse) of 248 nm laser light. [b] The concentration of ferricyanide was 0.25 mM; this value is such that the absorbance of the substrate at 248 nm (OD(*p*-Xy)/cm = 0.3) is higher than that of the oxidant.

$SO_4^{\bullet-}$. On radiolysis of aqueous solutions, $OH^\bullet$ and e_{aq}^- are produced. The latter was reacted with $S_2O_8^{2-}$ to form $SO_4^{\bullet-}$ (eqn. (7)) which then oxidizes toluene to its radical cation (eqn. (4)), while $OH^\bullet$ is scavenged by excess *t*BuOH yielding the unreactive $Me_2C(OH)CH_2^\bullet$.

$$e_{aq}^- + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{\bullet-} \qquad (7)$$

$K_3Fe(CN)_6$ (5 mM) was added to the solutions under radiolysis in order to quantitatively oxidize the isomeric methylhydroxycyclohexadienyl radicals to the corresponding cresols.[34] The distribution of products obtained from the γ-radiolysis experiment (bottom row of Table 2) is in accord with the results of Eberhardt[28] and is equal to the results obtained by photolysis (top row). This means that the species produced in the two cases (by reaction with $SO_4^{\bullet-}$ and by biphotonic ionization) have similar properties. As already mentioned above, this situation is in contrast to that with benzyl alcohol where a $PhCH_2OH]^{\bullet+}/SO_4^{2-}$ ion *pair* as the reactive intermediate was postulated.[10] The difference in behavior between the two similar systems is suggested to be due to the longer lifetime (with respect to reaction with the nucleophile water) of $PhCH_3]^{\bullet+}$ as compared to the (slightly) less electron-rich $PhCH_2OH]^{\bullet+}$.

In the case of *p*-xylene (Table 3), 248 nm photolysis of aqueous solutions afforded 2,5-dimethylphenol, 4-methylbenzylalcohol, and 1,2-di(p-tolyl)ethane. (A second dimer was found in an even smaller amount. This dimer was identified by GC-MS[35] on the basis of the characteristic fragmentation pattern of its molecular ion.)

From a comparison with the data for toluene (Table 2), it is evident that, in going from toluene to *p*-xylene, the deprotonation reaction becomes more important. This is expected on statistical grounds (in *p*-xylene, there are *two* methyl groups). Furthermore, due to electron donation by the second methyl, the radical cation of xylene should be less electrophilic than that of toluene. A third factor influencing the addition/elimination (= deprotonation) pattern is steric hindrance of the water addition by the additional methyl group.

2. Benzyl alcohols, $ArCH_2OH$

2.1 Time-resolved experiments

Direct photoionization. The experiments with $ArCH_2OH$ involved the same approach as employed with the methylbenzenes. In all cases, direct 248 nm photolysis led to the formation of the broad band of e_{aq}^-, in a biphotonic process, as in the case of the methylbenzenes. The lifetimes of the radical cations were determined using the dc-conductance technique. The results from the photoionization experiments are collected in Table 4, together with the results obtained from the use of $SO_4^{\bullet-}$ to produce the radical cations.

From the data in Table 4 it is evident that additional methyl groups, especially if present in the *para*-position, increase the lifetime of the benzyl alcohol-type radical cation. If compared with the family of methylbenzenes (see Table 1), it is clear that the hydroxymethyl group, CH_2OH, is considerably less "stabilizing" than the methyl group. This may be due to its weaker electron donation power ($\sigma_{CH_2OH} = 0.02$) as compared to the methyl group ($\sigma_{CH_3} = -0.14$) or to the greater tendency for C_α-deprotonation of the radical cation. Furthermore, it is evident that replacement of the methyl group by the methoxy group leads to an enhancement of the lifetime of the radical cation by up to 4–5 orders of magnitude.[37] In addition to the increase of electron density resulting from the methoxy group the reason for this is the fact that deprotonation from this group is not possible.

Reaction with $SO_4^{\bullet-}$. As in the case of the methylbenzenes, the attempt was made to produce radical cations from the benzyl alcohols by reaction with $SO_4^{\bullet-}$. For example, photolysis of a deoxygenated solution of peroxydisulfate (see eqns. (3) and (4)) in the presence of 4-methylphenethylalcohol resulted in the absorption spectra shown in Fig. 5 (recorded 50, 150 and 350 ns and 1 µs after the pulse).

At 50 ns after the pulse, the broad peak at 450 nm is mainly due to the radical cation. At 150 ns the spectrum shows strong absorption in the region between 250 and 320 nm whereby two peaks can be distinguished, one with λ_{max} 300 nm, assigned to

Table 4 Decay rates of methylated benzyl alcohol and phenethyl alcohol radical cations in aqueous solution. Comparison with the methoxylated counterparts (values in brackets)

Alcohol	k/s^{-1} [a]	
	Conductance[b]	Optical[c]
Benzyl alcohol	$\geq 5 \times 10^7$ [d]	—
4-Methylbenzyl alcohol	$\geq 5 \times 10^7$	—
4-Methoxybenzyl alcohol	(1.5×10^4)[e]	—
2,5-Dimethylbenzyl alcohol	1.4×10^6	1.6×10^6
2,4,6-Trimethylbenzyl alcohol	1.8×10^7	—
2-Phenylethanol	$\geq 5 \times 10^7$	—
2(4-Methylphenyl)ethanol	4.9×10^6	3.8×10^6
2(4-Methoxyphenyl)ethanol	(5.2×10^2)[f]	—
Cumyl alcohol	$\geq 5 \times 10^7$	—
4-Methylcumyl alcohol	1.8×10^7	
4-Methoxycumyl alcohol	(2.9×10^2)[e]	

[a] Accuracy: ±10%. [b] Determined at pH = 4.5 in the presence of 1% (v/v) 2-chloroethanol (to scavenge e_{aq}^-). The values in brackets are from the corresponding *p*-methoxybenzyl alcohols. [c] Obtained by monitoring the decay of the radical cation formed by reaction with $SO_4^{\circ-}$ at its λ_{max}. [d] From ref. 10. [e] From ref. 36 [f] From ref. 14

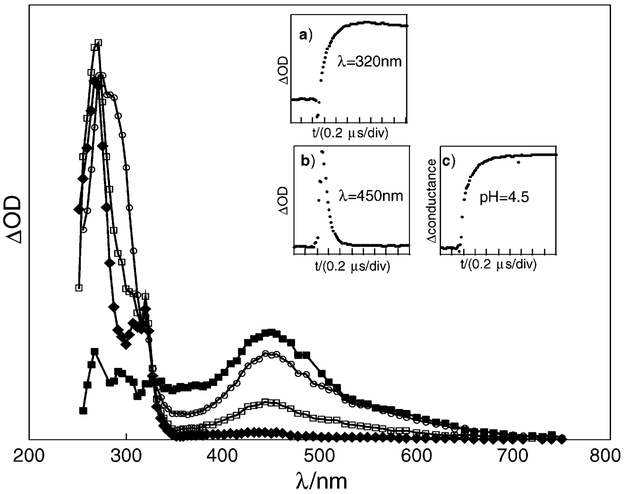


Fig. 5 Time-resolved absorption spectra observed on photolyzing a deoxygenated 70 mM solution of $K_2S_2O_8$ in water in presence of 5 mM 4-$MePhCH_2CH_2OH$: 50 ns (■); 150 ns (○); 350 ns (□); 1 μs (◆) after the pulse. Insets: (a) build up of the benzyl radical, (b) corresponding decay of the radical cation at 450 nm and (c) the resulting change of conductance at pH = 4.5 in the presence of 1% 2-chloroethanol.

a band of the radical cation, to which also the remaining absorption at 450 nm belongs, and the other with λ_{max} 268 nm due to the benzyl radicals formed from the radical cation *via* C_α–C_β or C–H fragmentation (see Scheme 3). At 350 ns after the pulse the absorptions due to the radical cation have to a large extent disappeared while the absorbances at 268, 310 and 322 nm, assigned to the benzyl radical, have increased. The assignments were confirmed by addition of oxygen to the solution: In agreement with the general behavior of radical cations, the bands assigned to the radical cation were not affected by O_2, whereas the benzyl radicals decayed rapidly.

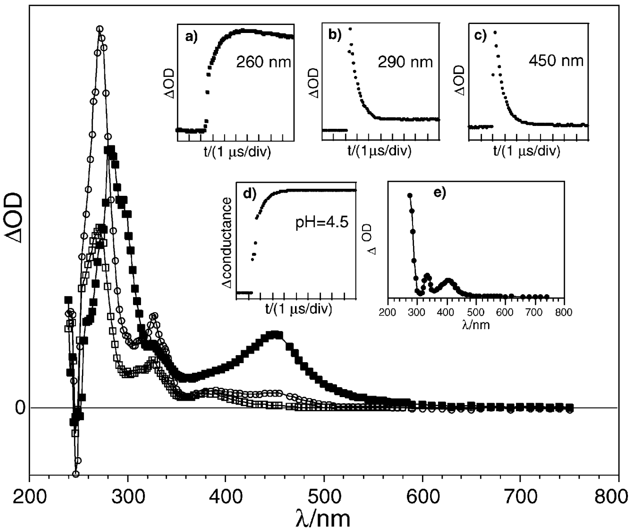
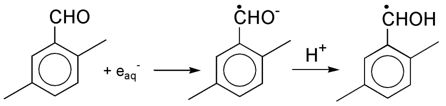
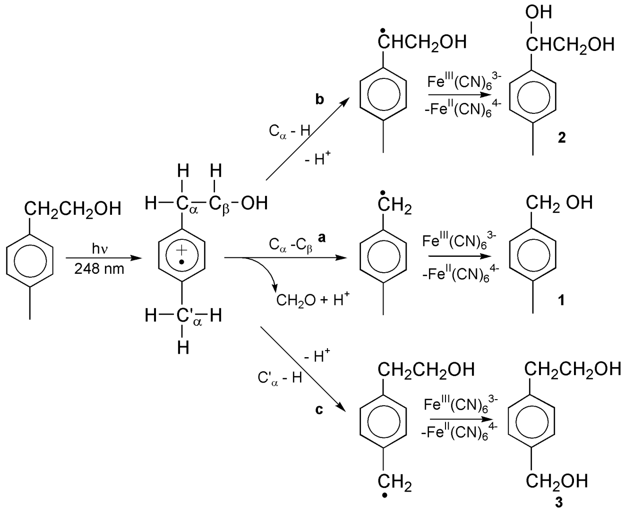


Fig. 6 Absorption spectra recorded 0.5 (■), 1.5 (○) and 14 μs (□) after 248 nm flash photolysis of an Ar-saturated aqueous solution of $K_2S_2O_8$ (70 mM) and 2,5-dimethylbenzylalcohol (5 mM). Insets: build-up of the benzyl radical (a), decay of the radical cation at 290 nm (b) and at 450 nm (c); and (d) the conductance change at pH = 4.5 following direct photolysis. In inset (e) is shown the spectrum of the 2,5-dimethyl-α-hydroxybenzylradical produced (see text) by reaction of 2,5-dimethylbenzaldehyde (0.5 mM) with the radiation-chemically produced e_{aq}^- at pH = 4.2 (*t*-BuOH 0.1 M).

Another example is 2,5-dimethylbenzyl alcohol. In Fig. 6 is shown the spectrum recorded on reaction with $SO_4^{\bullet-}$. Evident immediately after the pulse (at 0.5 μs) are the peaks of the radical cation at ≈450 and 280 with a shoulder at 330 nm. At 1.5 μs after the pulse the 450 and 280 nm peaks have disappeared to give rise to a strong peak at 272 nm and a smaller one at 328 nm. At this time there is also a weak and broad absorption in the region ≈380 nm (more visible 14 μs after the pulse). The bands at 272 and 328 nm are assigned to a mixture of the three different possible benzyl-type radicals formed from the radical cation *via* side-chain deprotonation (*i.e.*, the 2,5-dimethyl-α-hydroxybenzyl radical and the 2- or 3-hydroxymethyl-4-methylbenzyl radical). Of these, an "authentic" spectrum of the 2,5-dimethyl-α-hydroxybenzyl radical was obtained by reacting e_{aq}^- with 2,5-dimethylbenzaldehyde at pH = 4.2 with e^-_{aq} (eqn. (8)), in a pulse radiolysis experiment.

 (8)

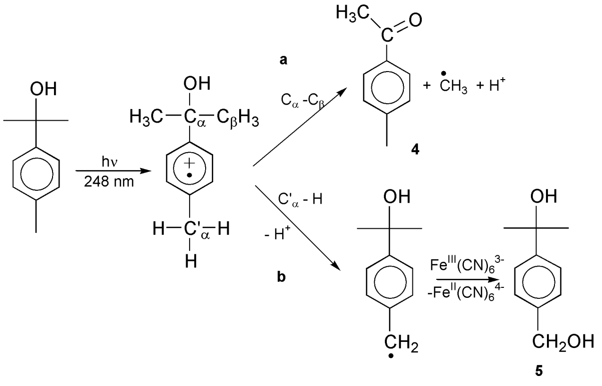
The spectrum, shown in Fig. 6, inset (e), is characterized by three bands: a strong one with a λ_{max} below 280 nm and two less intense peaks at 330 and 404 nm. From the difference of this spectrum from the one of Fig. 6 obtained 14 μs after the pulse (λ_{max} = 278 and 320, 330 and 380 nm) it can be concluded that the deprotonation of the radical cation does not proceed in an *exclusive* way from the OH-substituted carbon (giving the radical from eqn. (8)) but that there is also deprotonation from the methyl group(s) on the ring.



Scheme 3

2.2 Photolysis products. To check the mechanistic conclusions drawn in section 2.1, product analysis experiments were carried out, with conditions similar to those used for the "toluenes". As a general procedure, 5 mM aqueous solutions of the substrate containing 0.5 mM $K_3Fe(CN)_6$ (to oxidize the OH-adduct(s) expected to be formed by hydration of the radical cations) were photolyzed with 1000 pulses (150–200 mJ per pulse) of unfocussed 248 nm light and the resulting products, after extraction of the aqueous solutions with ether, were analyzed by GC/MS.

In the case of 4-methylphenethylalcohol, 4-methylbenzylalcohol (**1**, see Scheme 3) was the major product, showing that C–C fragmentation [reaction (a)] is an important process. Two minor products were identified on the basis of their mass spectra[38] as 1,2-dihydroxy-(4-methylphenyl)ethane (**2**) and 2-(4-hydroxymethylphenyl)ethanol (**3**).[39] Together with the time-resolved data reported above and the observation that a phenol-type product was not formed, these results are interpreted in terms of Scheme 3.



Scheme 4

Compared to elimination [steps (a)–(c)], the hydration reaction [analogous to step (**a**), Scheme 2] is apparently unimportant.

In the case of 4-methylcumyl alcohol the major products are 4-methylacetophenone (**4**) and 4-hydroxymethylcumyl alcohol (**5**) (the latter identified only on the basis of its mass spectrum[40]) showing that, again, hydration of the radical cation (addition) cannot compete with elimination). The results are rationalized in Scheme 4.

Summary and conclusions

The lifetimes and, in part, absorption spectra and reaction products of the radical cations produced biphotonically from methylated benzenes and benzyl alcohols in aqueous solution were determined by time-resolved laser spectroscopy. As expected, the lifetimes increase strongly with increasing number of additional methyl groups, the tendency for deprotonation from a methyl or hydroxymethyl group compared to addition (of water) to a ring position apparently increasing in this direction. In the case of toluene the radical cation appears to react as a free (solvated) ion, an observation which is in contrast to that[10] of benzyl alcohol where the reaction period is of the order of ion solvation (10–100 ps). The conclusion is that the lifetime τ of the toluene radical cation is between 10–100 ps and 20 ns. It would be interesting to compare this lifetime with that of corresponding carbenium ions. (With *small* radical cations, their reactivity has been shown to be intrinsically cationic rather than "radical" (M. Mohr and H. Zipse, *Phys. Chem. Chem. Phys.*, 2001, **3**, 1246).) A further conclusion is that, as compared to *methoxylated* analogues, the methylated benzyl alcohol radical cations are much more reactive, such that OH^--induction of side-chain fragmentation, as often required with methoxylated benzyl alcohol-type radical cations,[37] is not necessary.

Experimental section

Materials

All chemicals of the purest grade available (Aldrich and Merck) were used as supplied except for toluene, *o*-xylene, *m*-xylene and *p*-xylene (*p*-Xy) which were purified by chromatography over basic Al_2O_3. The water used was from a MilliQ-Millipore system.

p-Methylcumylalcohol

p-Methylcumylalcohol (2-(4-Methylphenyl)propan-2-ol) was prepared *via* a Grignard reaction involving 10.3 g of *p*-bromotoluene and 1.4 g of magnesium turnings in 30 ml of anhydrous tetrahydrofuran. To the resulting *p*-tolylmagnesium bromide was added in a dropwise fashion (over a period of 30 min) a solution of 3.3 g of acetone in 40 ml of THF. The basic magnesium bromide was then decomposed by addition of 140 ml of 40% NH_4Cl in water. The solution was extracted with ether and the combined ethereal samples were dried over anhydrous Na_2SO_4. The ether was evaporated and the crude product purified by elution through a SiO_2 column with a petroleum ether/ethyl acetate mixture. The yield was 5.3 g (76%); ^1H NMR ($CDCl_3$) δ 7.4–7.1 (m, 4 H, ring H), 2.3 (s, 3 H, *p*-CH_3), 1.7 (s, 1 H, OH), 1.6 (s, 6 H, $C(CH_3)$) ppm.

Laser flash photolysis

The laser flash photolysis (LFP) experiments were carried out using a Lambda Physik EMG103MSC excimer laser which produces 20 ns pulses (10–180 mJ per pulse) of 248 nm light (KrF^*). The optical absorption or conductance signals was digitized with Tektronix 7612 and 7912 transient recorders interfaced with a DEC LSI $11/73^+$ computer which also process-controlled the apparatus and on-line pre-analyzed the data. Final data analysis was performed on a Microvax I connected to the LSI. The solutions were deoxygenated by bubbling with argon and flowed through a 2 mm (in the direction of the laser beam) by 4 mm (in the direction of the analyzing light) Suprasil quartz cell. Direct photoionization was performed using saturated solutions[41] of methylbenzenes (OD/cm 0.1–0.4 at 248 nm) or 2–5 mM solutions of the benzyl alcohols (OD/cm $\approx$ 0.6–0.9 at 248 nm). For one-electron oxidation with $SO_4^{\bullet -}$ the concentration of added $K_2S_2O_8$ (typically 70 mM) was such that this component absorbed most of the 248 nm light.

Product analysis

Saturated solutions of the methylbenzenes were deoxygenated by bubbling with Ar (saturated with the aromatic) and photolyzed with 1000 pulses (20 ns, 150–200 mJ per pulse) of 248 nm laser light. The solutions contained $K_3Fe(CN)_6$ (0.25 mM, OD/cm = 0.2 at 248 nm) in order to oxidize any photo-generated hydroxycyclohexadienyl radicals into phenols. After irradiation an internal standard was added to the solutions (*e.g.* for toluene, 0.1 mM 4-methylbenzaldehyde), they were extracted with diethyl ether and, after concentration to a small volume, analyzed by GC with flame ionization detection (HP 5890 gas chromatograph with a 30 m Stabilwax column, H_2 as carrier gas, 100–250 °C). The products were identified by comparison with authentic compounds, except in the case of some of the lower-yield products where GC-MS was used to establish their structure. Blank experiments using non-exposed samples were always carried out. The same procedure was followed in the case of the benzyl alcohols (5 mM substrate, 0.5 mM $K_3Fe(CN)_6$), except for the GC where a HP 5890 gas chromatograph with a 15 m Stabilwax column was used.

Solutions were also irradiated (2 h) with the light of a medium-pressure mercury vapor lamp (Philips HPK 125 W/L) and analyzed as above.

Radiolysis was carried out with a ^{60}Co-γ-source at a dose rate of 0.5 Gy s^{-1} on the following aqueous solution: 6 mM toluene, 2 mM $K_2S_2O_8$, 1 M *t*BuOH and 0.5–5 mM $K_3Fe(CN)_6$. The irradiation time was chosen to obtain a 40% conversion of peroxydisulfate.

Pulse radiolysis

Pulse radiolysis (PR) experiments were performed with a 2.8 MeV van de Graaff electron accelerator delivering 300 ns pulses[42] with doses such that 0.5–3 μM radicals were produced.

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30 The rate constant for this reaction was determined by producing the benzyl radical by photolysis of phenylacetone in the presence of $K_3Fe(CN)_6$ and monitoring its rate of depletion to be of the order 10^9 M^{-1} s^{-1}.

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32 Three peaks with different retention times but with similar mass spectra were found. For the most intense peak: $M = 110$, m/z (relative abundance): 65 (25), 77 (35), 91 (85), 05 (100), 109 (20).

33 This reaction is analogous to the well-studied (L. Kaplan, L. A. Wendling and K. E. Wilzbach, *J. Am. Chem. Soc.*, 1971, **93**, 3821–3822; L. A. Kaplan, D. J. Rausch and K. E. Wilzbach, *J. Am. Chem. Soc.*, 1972, **94**, 8638–8640) photooxidation of aqueous benzene.

34 The second-order rate constant for this reaction was determined in a LFP (248 nm) experiment, monitoring the rate of decay of $Fe(CN)_6^{3-}$ at 420 nm, to be 2.0×10^8 M^{-1} s^{-1}. That this value is considerably higher than that given (V. Madhavan and R. H. Schuler, *Radiat. Phys. Chem.*, 1980, **16**, 139–143) for the *un*substituted hydroxycyclohexadienyl radical is probably due to the higher electron density in the methyl-containing radical.

35 $M = 210$, m/z values (relative abundances): 195 ((100), 180 (29), 165 (26), 118 (63)) as (2,5-dimethyl(4-methylbenzyl)benzene) and, finally, traces of 4-methylbenzaldehyde were found as products.

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39 2,3-Bis(4-methylphenyl)propane-1-ol, 2,3-bis(4-methylphenyl)butane-1,2-diol and 4-methylbenzaldehyde were found in traces. The former two are the dimerization products of the primary radicals formed in steps (a) and (b), whereas 4-methylbenzaldehyde is a secondary product, derived from **1**.

40 From the mass spectrum of 4-hydroxymethylcumylalcohol: $M = 166$, m/z values (relative abundance): 151 (27), 148 (14), 133 (6), 107 (7), 91 (4), 77 (10).

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