Comparison of reactions of radical cations of 1-phenylalkanols produced by photoionization and by one-electron oxidation in aqueous solution

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Benzyl alcohols in aqueous solution react with photo- and radiation-chemically produced $^{\bullet}OH$ and $SO_4^{\bullet-}$ radicals with diffusion-controlled rates to yield OH-adducts and benzyl alcohol radical cations, respectively. The former can be converted to the radical cations by H^+-induced (heterolytic) dehydroxylation, whereas the latter decay by a) electrophilic reaction with water (= reverse of the dehydroxylation reaction) giving rise to $C_{nucleus}$–OH-adducts and by b) side chain C–H deprotonation yielding α-hydroxybenzyl-type radicals. If, however, the radical cation is produced by biphotonic ionization of the benzyl alcohol, the pattern of $C_{nucleus}$–OH bond formation and side chain C–H bond breakage is different from that in the reaction with $SO_4^{\bullet-}$. It is concluded that, at least in this reaction, it is not the free, solvated radical cation that reacts with water but the ion pair [radical cation–SO_4^{2-}].

Introduction

Radical cations of aromatics whose gas-phase ionization potential (IP) is close to that of benzene (9.25 eV) tend to have a high degree of reactivity in solution, and even with nanosecond detection techniques it is typically not possible to observe these species directly. The nature of the one-electron oxidized species therefore has to be deduced from their reaction products, and this sometimes introduces ambiguities. Due to the high reactivity of these radical cations, even their sufficiently rapid formation becomes a problem. Obviously, in order to obtain a radical cation, the process of electron removal from the parent must be shorter than the radical cation's lifetime. This requires powerful one-electron acceptors (oxidants) and polar solvents.[1]

Furthermore, radical cations of electron-poor systems are usually strong electrophiles. On the other hand, polar solvents, which are an essential prerequisite for electron transfer processes to occur rapidly, are often nucleophilic and thus tend to destroy the radical cations by chemical reaction. A good example of such a solvent is water. Nucleophilic attack of a radical cation by the solvent can easily be faster than its formation, particularly if the latter is a bimolecular process whose rate is of course determined by the concentration of substrate, which is usually smaller than that of solvent. A (quasi)unimolecular method of producing a radical cation is therefore desirable, and photoionization (PI) is, in principle, a method to achieve this goal.

Photoionization has, in fact, been extensively used in the past to produce one-electron oxidized species. With electron-rich molecules such as, *e.g.*, N,N,N',N'-tetramethyl-*p*-phenylenediamine, PI is typically a mono-photonic process with quantum yields often >10%,[2–4] and these types of radical cations[5] are usually long-lived. As the electron density of the molecules is decreased, mono-photonic ionization tends to become less efficient, if not thermodynamically impossible, unless the photon energy of the exciting light is very high (*e.g.*, >200 kcal mol^{-1} (which corresponds to a photon of 143 nm) for molecules with gas-phase IP of *ca.* 9 eV).

A way to photoionize molecules with a "normal" IP of *ca.* 9 eV (such as benzene) without using vacuum UV light is by biphotonic excitation,[6,7] for instance with 248 nm quanta.[8–12] If ionization is the dominant photochemical process, this

method has great potential for studying highly reactive radical cations, since in practice their formation rate is limited only by the temporal width of the exciting light pulse. A particularly interesting aspect is that under these conditions the radical cations may have a very special 'counter-anion', namely the (solvated) electron.

So far the method of producing radical cations by biphotonic ionization, and the nature of the reaction products, have not been systematically studied. We felt this was, therefore, necessary, and decided to take a look at benzyl alcohol and some of its derivatives. This family of compounds has been thoroughly studied under one-electron oxidizing conditions using product analysis[13–15] and also the method of electron paramagnetic resonance has been applied, and, as a result, the nature of the radicals that exist on the ms time scale is well established.[16–21]

In the very polar and quite nucleophilic solvent water, radical cations of mono-substituted benzenes have been observed only with the electron-rich systems anisole,[22,23] thioanisole[24] or N,N-dimethylaniline.[25] With toluene, however, only products of the hypothetical radical cation were seen, *i.e.*, the benzyl radical in strongly acidic solutions[26,27] (produced by deprotonation of the radical cation from the methyl group) and (isomeric) methyl-hydroxycyclohexadienyl radicals (formed by hydroxylation by water of the radical cation) in neutral solutions.[28–31]
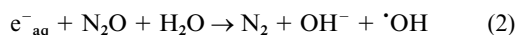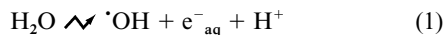
On the basis of the Hammett σ-constant of hydroxymethyl as compared to methyl, the radical cation of benzyl alcohol[32] should be more difficult to produce and more reactive than that of toluene. Nonetheless, benzyl alcohol has the advantage of possessing good solubility in water, permitting experiments to be performed in a more controlled way. We therefore decided to take a look at benzyl alcohol with the aim of studying its radical cation.
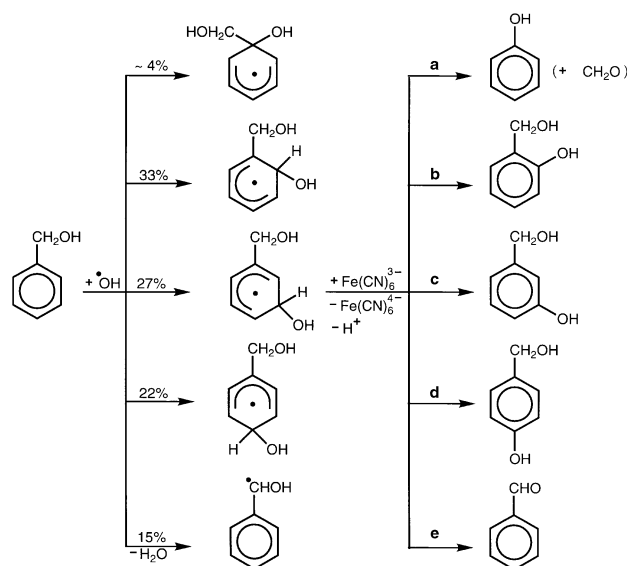
Results and discussion

1. Pulse radiolysis and laserflash photolysis results

a) The reaction of $^{\bullet}OH$. This was investigated since it yields the same hydroxycyclohexadienyl ($\equiv$ HCHD) radicals (although in a different proportion, see later) as those from water addition to the radical cation. N_2O-Saturated aqueous solutions at

pH ≈ 6 that contained 0.1–0.5 mM benzyl alcohol or its side-chain substituted derivatives $PhCR^1(R^2)OH$ ($R^1 = H$, $R^2 = H$, Me, Et, CH_2OH, CO_2H; $R^1 = R^2 = Me$) were irradiated with 100 ns pulses from a 3 MeV electron accelerator. Irradiation of water [eqn. (1)] produces OH-radicals and the hydrated electron, e^-_{aq}, which can be converted to an additional $^\bullet OH$ by reaction with N_2O [eqn. (2)].

$$H_2O \rightsquigarrow {}^\bullet OH + e^-_{aq} + H^+ \qquad (1)$$

$$e^-_{aq} + N_2O + H_2O \rightarrow N_2 + OH^- + {}^\bullet OH \qquad (2)$$

In the presence of 0.1–2 mM of the substrates, the OH-radicals produced by the pulse are scavenged in ≤2.5 µs to mainly yield (by addition to the ring) isomeric HCHD radicals and, to a minor extent (by H-abstraction from the benzylic position), α-hydroxybenzyl radicals (see later). The observed spectra (not shown) have intense bands with $\lambda(max) \approx 320$ nm and, except for the case of α,α-dimethylbenzyl alcohol, weaker bands at ~270 nm. The 320 nm bands are assigned to the isomeric (hydroxymethyl)hydroxycyclohexadienyl radicals ("OH adducts") formed by addition of $^\bullet OH$ to the ring, and the 270 nm band to the α-hydroxybenzyl radicals produced by H-abstraction from the CH_2OH group (see Scheme 1 and

Fig. 1 Absorption spectra of the transients [recorded at 250 ns (○), 1 µs (●), 1.5 µs (△), and 3 µs (▲) after the 248 nm pulse] from the reaction of $^\bullet OH$ (generated by photolysis of 0.1 M H_2O_2) with 1 mM benzyl alcohol in 1 M $HClO_4$. In the left inset is shown the increase of absorption at 268 nm due to formation of $PhC^\bullet(Me)OH$ from the "OH-adduct" in a 2 mM solution of 1-phenylethanol containing 0.2 M H_2O_2 and 2 M $HClO_4$. From the inset to the right it is evident that the rate of formation of $PhC^\bullet(Me)OH$ from the "OH-adduct" increases with increasing acidity of the aqueous solution.

the 248 nm light is predominantly absorbed by the H_2O_2 which undergoes homolysis yielding two OH radicals [eqn. (3)] which then react with the organic substrate.

$$H_2O_2 \xrightarrow{h\nu} 2\,{}^\bullet OH \qquad (3)$$

The advantage of this method is that the yield of $^\bullet OH$ is pH-independent below pH ≈ 3, which is not the case with radiation-chemically produced $^\bullet OH$ in N_2O-saturated aqueous solutions, where the $^\bullet OH$ yield decreases due to competition between N_2O and H^+ for e^-_{aq} ($e^-_{aq} + H^+ \rightarrow H^\bullet$). As a result of this reaction, in the radiation-chemical experiment, below pH ≈ 3 the yield of $H^\bullet$ becomes comparable to that of $^\bullet OH$. Like $^\bullet OH$, H-atoms react with aromatics by addition and the so-formed cyclohexadienyl radicals have very similar absorption spectra to those of the OH adducts.[37] However, the H adducts cannot be converted to α-hydroxybenzyl radicals by H^+-induced dehydroxylation and deprotonation [see eqn. (4)]. Therefore, in order to study, in the presence of large H^+ concentrations, the conversion of OH adducts without the interference from H adducts it is necessary to produce $^\bullet OH$ without the intermediacy of e^-_{aq}.

In Fig. 1 are shown the time-dependent absorption spectra measured on reacting 1 mM benzyl alcohol with $^\bullet OH$, produced by photolysis of 0.1 M H_2O_2, in the presence of 1 M $HClO_4$.

The spectrum recorded at 250 ns after the 20 ns, 248 nm pulse (○) shows a peak at 320 nm, due to the OH adducts, and a larger one at 270 nm, from the α-hydroxybenzyl radical.[38] In the acidic solution, after about 3 µs the α-hydroxybenzyl radical peak at 270 nm has considerably increased, at the expense of the OH adducts absorbing at 320 nm. There is a well-defined isosbestic point at 285 nm, indicating that the conversion of the two species is a 1:1 process. From the left inset (showing the case of 1-phenylethanol) it is evident that the increase of optical density (OD) at 268 nm, reflecting this conversion, follows exponential kinetics.

The conversion of the OH adducts to the α-hydroxybenzyl radicals is explained by H^+-induced heterolytic dehydroxylation with subsequent (or synchronous) deprotonation (or decarboxylation, C–C fragmentation)[39] of the (incipient) radical cation, e.g., in the case of deprotonation, eqn. (4):

Scheme 1

section 2). The 320 nm assignment is supported by the observation of similar spectra on reaction of $^\bullet OH$ with other simple benzene derivatives including benzene itself,[33–37] and the identification of the 270 nm band by its similarity with the spectra observed on photoreduction of benzaldehyde in propan-2-ol, on photocleavage of benzoin, on oxidative decarboxylation of mandelic acid, or on H^+ induced dehydroxylation of the OH adducts (see later). The observation that the 270 nm band is *absent* in the case of α,α-dimethylbenzyl alcohol (there is a *minimum* at 270 nm) is in agreement with this picture, since with this compound a benzyl radical can not be formed by H-abstraction.

The rate constants for the reaction of $^\bullet OH$ with benzyl alcohol and its derivatives were measured by monitoring the rate of buildup of the optical density (OD) at 320 nm as a function of the concentrations of the substrates in the range 0.05–0.5 mM. The second order rate constants so obtained are listed in Table 1. The values are all $(4–6) \times 10^9$ M^{-1} s^{-1}, which means the reactions are essentially diffusion controlled.

The transients described above could also be produced by 248 nm photolysis of H_2O_2 (e.g., 0.1 M) in the presence of, e.g., 0.1–1 mM of the benzyl alcohols. Under these conditions,
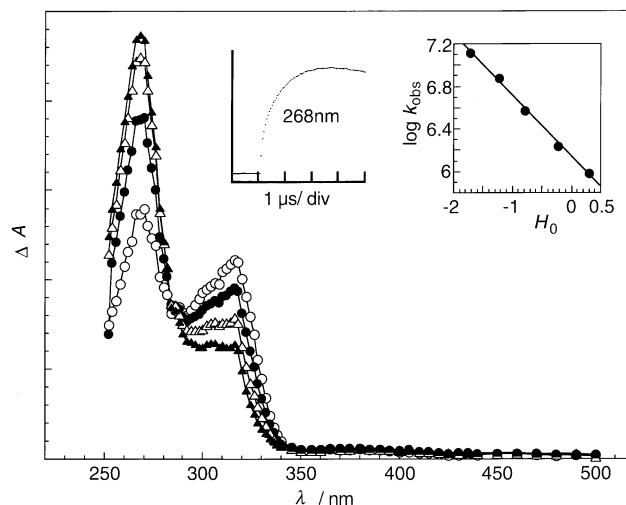
Table 1 Rate constants $k_{\cdot OH}$ and $k_{SO_4^{\cdot-}}$ for reaction of $^\cdot OH$ and $SO_4^{\cdot-}$ with 1-phenylalkanols in aqueous solution, [a] 20 °C

1-Phenylalkanol	λ_{obs} [b]/nm	$10^{-9}k_{\cdot OH}$/M^{-1} s^{-1}	λ_{obs} [b]/nm	$10^{-9}k_{SO_4^{\cdot-}}$/M^{-1} s^{-1}
Benzyl alcohol	320	6.4	270	3.2
1-Phenylethanol	320	6.4	270	3.3
1-Phenylpropanol	315	5.7	270	3.1
2-Phenylpropan-2-ol	320	4.3	320	2.1
Phenylethyleneglycol	320	4.5	270	2.6
Benzyl methyl ether	320	6.4	270	3.1
Mandelic acid	320	4.4	270	1.5

[a] At pH 5–7. [b] Wavelength of observation.
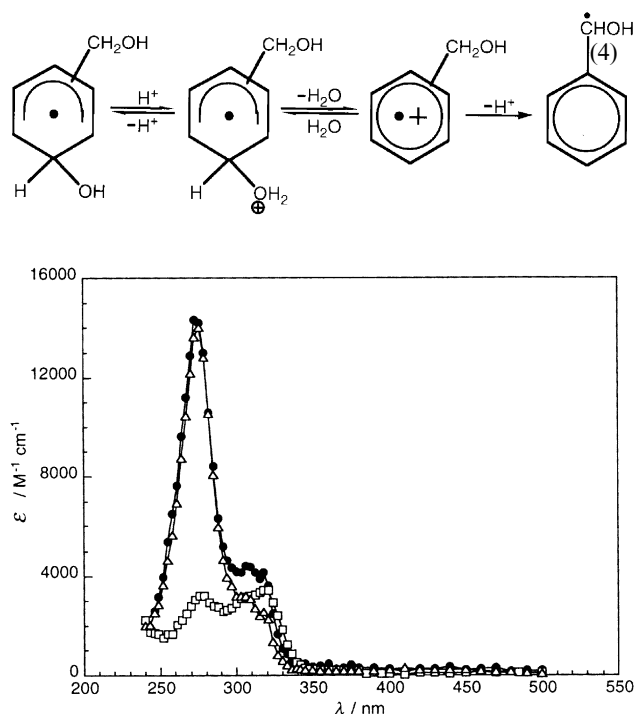
Fig. 2 Absorption spectra recorded at 20 µs on reaction of 1 mM PhCH$_2$OMe with $^\cdot OH$ (□), $SO_4^{\cdot-}$ (●), pH 6, or $O^{\cdot-}$ (△), 0.5 M KOH. The extinction coefficients are based on $G(^\cdot OH) = 6$, $G(SO_4^{\cdot-}) = 3$, and $G(O^{\cdot-}) = 6.6$.

In all cases (R = H, Me, Et, CO$_2$H, CH$_2$OH), the rate of PhC$^\cdot$ROH formation increased monotonously with increasing H$^+$ activity up to 5 M HClO$_4$, where it was ~5 × 10^7 s^{-1}. The rate constant for C–H deprotonation of the intermediately produced radical cations, k_{deprot}, must therefore be greater than this value. The sensitivity towards H$^+$, as measured by the slope of the log k(formation of PhC$^\cdot$(OH)R) *vs.* H_0 dependence, increases in the series R = CO$_2$H, H, CH$_2$OH, CH$_3$, CH$_2$CH$_3$, *i.e.* with increasing electron donating power of R, as shown in Table 2.[40]

Benzyl methyl ether. The OH radical (produced radiation- or photo-chemically) was also reacted with benzyl methyl ether, for comparison with the behavior of the benzyl alcohols. The spectrum observed at pH 6 (see Fig. 2) consists of two peaks: one at 320 nm and a second one, which is only slightly less intense, at 270 nm.

The former is assigned to the isomeric (methoxymethyl)-hydroxycyclohexadienyl radicals formed by addition of OH to the ring, the latter to the α-methoxybenzyl radical, produced by H-abstraction from the benzylic carbon. This assignment is corroborated by the changes that occur on reacting the OH-adduct radicals with H$^+$: as in the case of benzyl alcohol, at 1 M HClO$_4$ the peak at 320 nm disappears rapidly, giving rise to more of the 270 nm species. That this is the α-methoxybenzyl radical was shown also by reacting O$^{\cdot-}$, produced by pulse radiolysis of an aqueous solution containing 0.5 M KOH, with
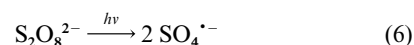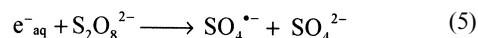
Table 2 Sensitivities for H$^+$-induced conversion of the OH-adducts of C$_\alpha$-substituted benzyl alcohols into α-hydroxybenzyl-type radicals [a]

Benzyl alcohol	Sensitivity (log k_{obs}/H_0)
PhCH(OH)CO$_2$H	0.41
PhCH$_2$OH	0.53
PhCH(OH)CH$_2$OH	0.54
PhCH(Me)OH	0.58
PhCH(Et)OH	0.58

[a] 1 mM Benzyl alcohol, 0.1 M H$_2$O$_2$, 0–5 M HClO$_4$, 248 nm photolysis, 20 °C.

the ether (saturated). The O$^{\cdot-}$ radical is known[41] to react by H-abstraction from the side chain, and not by addition to the ring. The resulting spectrum [Fig. 2 (△)] is almost identical to that (●) observed on reaction with $SO_4^{\cdot-}$ [(see section b), below] or on $^\cdot OH$ addition/H$^+$-induced dehydroxylation in 1 M HClO$_4$ (not shown) and is thus identified in terms of the α-methoxy-benzyl radical. The spectrum of this species has a shoulder at 310–320 nm, the region where the OH adducts also absorb. In this region, other benzyl radicals, including PhCH$_2^\cdot$, also have bands which are, however, considerably weaker than their main bands at 260–270 nm.

b) The reaction of $SO_4^{\cdot-}$. The radical $SO_4^{\cdot-}$ was produced radiation-chemically, eqn. (5), and by photolysis, eqn. (6), in a manner analogous to $^\cdot OH$ generation:

$$e^-_{aq} + S_2O_8^{2-} \longrightarrow SO_4^{\cdot-} + SO_4^{2-} \qquad (5)$$

$$S_2O_8^{2-} \xrightarrow{h\nu} 2\,SO_4^{\cdot-} \qquad (6)$$
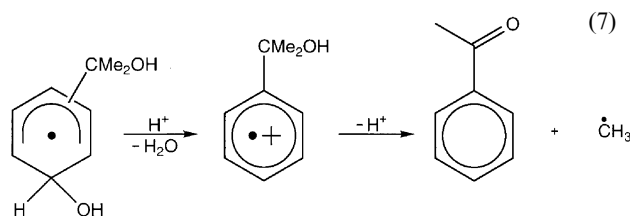
In the photochemical experiments the concentrations of the organic substrates were high enough to enable $SO_4^{\cdot-}$ to be rapidly scavenged, but low enough to ensure that >;90% of the 248 nm light was absorbed by the $S_2O_8^{2-}$ ion. In Fig. 3 are shown the spectra measured after completion of the reaction of $SO_4^{\cdot-}$ with benzyl alcohol, benzyl methyl ether, and α,α-dimethylbenzyl alcohol at pH 6–7. In the first two cases, there are pronounced peaks at 260–270 nm and quite weak bands (or shoulders) at 320 nm. In the last case only a band at 320 nm is visible, whereas at 270 nm there is a minimum. As pointed out in the previous paragraph, the 270 nm band is due to α-hydroxy- or methoxy-benzyl radical and the 320 nm absorption to OH adducts. With the exception of α,α-dimethylbenzyl alcohol (DMBA), the amplitude of the 320 nm peak can be reduced by reacting $SO_4^{\cdot-}$ with the substrates in the presence of H$^+$. The reduction in the OD at 320 nm led to an increase in that at 270 nm, indicating that the reaction of the OH adducts with H$^+$ gives rise to benzyl radicals, obviously by heterolytic dehydroxylation, eqn. (4). At, *e.g.*, 0.1 M H$^+$ the conversion of the OH adducts took place in a few µs.

In the case of DMBA, the 320 nm band was found to disappear in an H$^+$ catalyzed process *without* giving rise to a product band. This observation is in agreement with the conversion of the aromatic OH adduct radical to the aliphatic
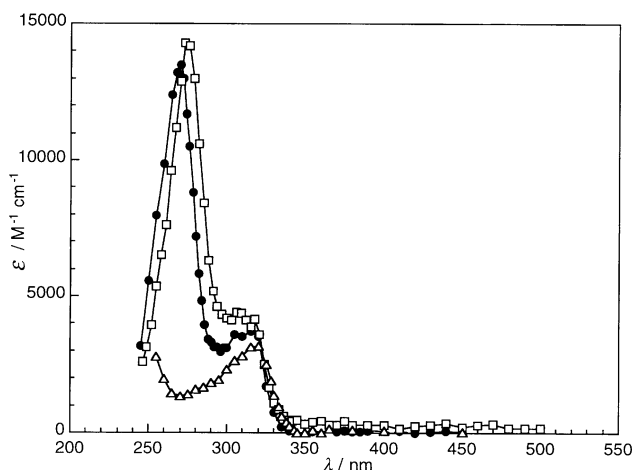
Fig. 3 Absorption spectra recorded at 10 µs after production of $SO_4^{\cdot-}$ [*via* eqn. (5)] in the presence of 1 mM benzyl alcohol ($\bullet$), benzyl alcohol methyl ether ($\square$), or α,α-dimethylbenzyl alcohol ($\triangle$) at pH 6–7. The solution contained 2 mM $K_2S_2O_8$ and 0.1 M *tert*-butyl alcohol. To obtain the extinction coefficients, G(radical) was assumed to be equal to $G(SO_4^{\cdot-}) = 3.0$.

Fig. 4 Absorption spectrum measured on 248 nm photolysis of a 1 mM aqueous solution of benzyl alcohol, pH 6, $\square$. For comparison are shown the spectra obtained on addition of 0.2 M H_2O_2 and 3 M $ClCH_2CH_2OH$ and 0.5 M $HClO_4$ ($\blacktriangle$) or on addition of 0.2 M $(NH_4)_2S_2O_8$ ($\bigcirc$). All spectra have been normalized to the peak at 270 nm.

methyl radical, a proton, and acetophenone, [eqn. (7)], as concluded from EPR[21] and product[13] measurements.

(7)
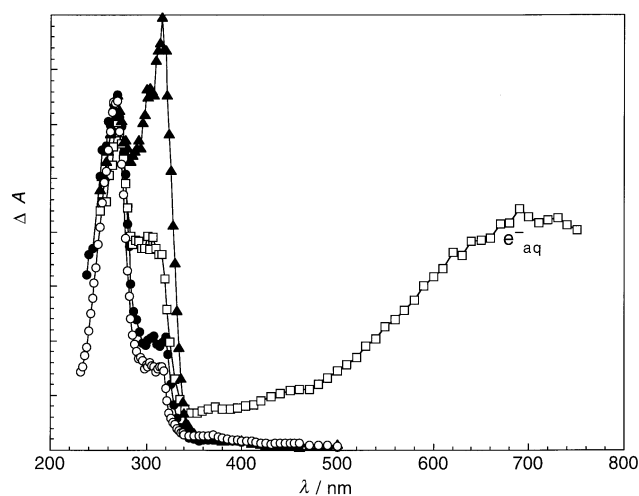
c) Direct 248 nm photolysis. The substrates were also photolyzed directly, *i.e.*, with 248 nm light and in the absence of H_2O_2 or $S_2O_8^{2-}$. Photolysis of, *e.g.*, benzyl alcohol at pH 6–7 led to the production of e^-_{aq},[42] as evident (monitored) in the wavelength region 600 to 750 nm (see Fig. 4, squares. All the spectra are normalized to the peak at 260–270 nm). In addition to the broad band of e^-_{aq} with a maximum at ~720 nm, there is a shoulder at ~310 nm, which is assigned to the isomeric (hydroxymethyl)hydroxycyclohexadienyl radicals ("OH-adducts"), and a sharp peak at 260 nm, which is mainly due to the α-hydroxybenzyl radical (see later). On scavenging the electron with 3 M 2-chloroethanol and adding 0.5 M $HClO_4$, the shoulder at 310 nm becomes considerably smaller, and the 260 nm band (spectrum with full circles) is increased. This spectrum is very similar to that recorded on reaction of $SO_4^{\cdot-}$ with benzyl alcohol (open circles). That the shoulder at 310 nm is due to the OH-adducts is evident from comparison with the spectrum recorded on reaction of $\cdot OH$ with benzyl alcohol (triangles).
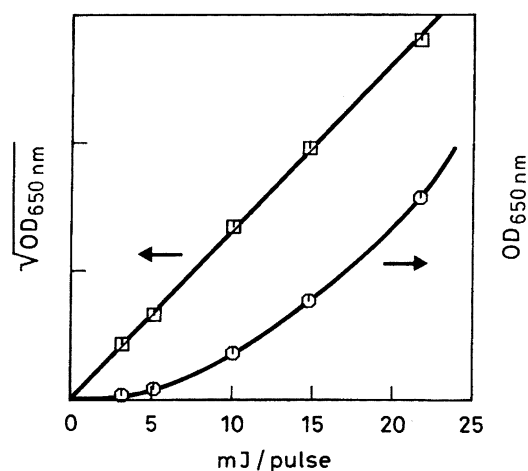
The yield of e^-_{aq} increased with the intensity of the laser light (measured as mJ per pulse) in a quadratic fashion (see Fig. 5), which demonstrates the involvement of *two* light quanta in the ionization process.

2. Product analysis results

Aqueous solutions (N_2O saturated) containing 10 mM benzyl alcohol and 1–8 mM $K_3Fe(CN)_6$ were ^{60}Co-γ-irradiated with doses such that conversion was kept below 1%. GC with FID was used for qualitative, and HPLC with optical and electrochemical detection for quantitative product analysis. *o*-, *m*-, and *p*-Hydroxybenzyl alcohol, phenol, and benzaldehyde were found as reaction products (see Table 3 and Scheme 1). Similar γ-radiolysis experiments were performed with $S_2O_8^{2-}$ as a source of $SO_4^{\cdot-}$ radicals [eqn. (5)]. Furthermore, benzyl alcohol

Fig. 5 Dependence of the yield of e^-_{aq} (as monitored at 650 nm) on the laser ($\lambda = 248$ nm) pulse power in a 1 mM aqueous solution of benzyl alcohol at pH 6.

was directly photolyzed in solutions additionally containing 1–2 mM $Fe(CN)_6^{3-}$ (to oxidize hydroxycyclohexadienyl and benzyl-type radicals formed as a result of the photolysis). Under these conditions, the percentage of the 248 nm light absorbed by the benzyl alcohol was >95%. These results are presented in Table 3.

a) The reaction of $\cdot OH$ with benzyl alcohol. The results are explained by reactions (1) and (2) (production of $\cdot OH$) and Scheme 1 (formation and oxidation of the organic radicals). Among the products, the hydroxybenzyl alcohols account for about 85% of the initiating OH radicals (Scheme 1, reactions **b,c,d**). Phenol is produced with a yield of 4%, and its precursor is suggested to be the radical formed by addition of $\cdot OH$ at the *ipso*-position (reaction **a**).[43] In order to give phenol, the carbocation formed by one-electron oxidation must undergo C–C fragmentation with formaldehyde as the other product. Attempts to detect H_2CO were, however, unsuccessful in the presence of $Fe(CN)_6^{3-}$ (probably because H_2CO is oxidized by ferricyanide), and in its absence phenol was not formed.

Thus, the dominant reaction of $\cdot OH$ is addition to the phenyl ring (reactions **a–d**, Scheme 1), in agreement with previous studies.[33–36] The so-formed isomeric hydroxycyclohexadienyl radicals are then converted to the corresponding phenols by (formal) one-electron oxidation by $Fe(CN)_6^{3-}$ and C–H depro-

Table 3 Yields of products formed in the reaction of benzyl alcohol with $^{\bullet}OH$ and $SO_4^{\bullet-}$. Comparison with products from the 248 nm photolysis

| Initiating radical | Yield of product [a] | | | | | |
	2-Hydroxybenzyl alcohol [b]	3-Hydroxybenzyl alcohol [b]	4-Hydroxybenzyl alcohol [b]	Benzaldehyde [c]	Phenol [d]	Total yield [e]
$^{\bullet}OH$	32.6 (0.74)	26.7 (0.61)	22.0 ($\equiv$ 1)	14.6	3.7	99.6
$SO_4^{\bullet-}$	16.9 (0.49)	18.4 (0.53)	17.3 ($\equiv$ 1)	42.3	$\leq$3.4	$\leq$98.3
248 nm Photolysis	7 [f,g] (0.07)	8 [f,g] (0.08)	53 [f,g] ($\equiv$ 1)	31 [g]		

[a] In percent of the $^{\bullet}OH$ or $SO_4^{\bullet-}$ initially produced. $G(^{\bullet}OH)$ was taken to be 6 for the case of N_2O saturated solutions and $G(SO_4^{\bullet}) = 2.6$ for the argon saturated solutions which contained 1 mM $K_2S_2O_8$ and 50 mM *tert*-butyl alcohol. The error in the yields is estimated to be $\pm$10%. The pH was 3–8 for the case of $^{\bullet}OH$ and 6 for the case of $SO_4^{\bullet-}$. The numbers in parentheses are the relative yields per position on the benzene ring of benzyl alcohol. [b] Determined by optical and electrochemical detection. [c] Determined by optical detection. [d] Determined by electrochemical detection. [e] Relative to the depletion of the parent. [f] In the case of 248 nm photolysis, the concentration of products depends on the number of pulses (typically 1000 pulses) and the dose per pulse (typically 150 mJ per pulse). Thus, relevant here is only the ratio of the products. Signals from products other than those identified were $\geq$10 times weaker. [g] Molar ratio of products when conversion was $\leq$1%.

tonation of the resulting carbocation, a reaction type that is well documented.[36,44–46]

Corrected for the number of available positions, there is a clear preference for the addition of $^{\bullet}OH$ at the *para*-position, and even the *ortho* is favored over the *meta*-position. On this basis, with respect to the electrophilic $^{\bullet}OH$, the $HOCH_2$ substituent apparently behaves as a weakly electron-donating group.

The sum of the yields of phenols is 85%. The remaining 15% of the OH radicals react by H-abstraction from the benzylic carbon, and the resulting α-hydroxybenzyl radical is oxidized by $Fe(CN)_6^{3-}$ to give benzaldehyde (Scheme 1, reaction **e**). This relatively high percentage of H-abstraction as compared to the toluene case (H-abstraction <10%)[27,31] is in agreement with the analogous observations made on the basis of EPR measurements.[21] It indicates activation of the benzylic hydrogens by the OH group, an activation that is also observed with analogous aliphatic systems (see ref. 47 and references therein) and that is probably caused by stabilization of positive charge by the α-OH group in the ionic transition state of the H-abstraction process of $^{\bullet}OH$. Formation of the α-hydroxybenzyl radical is directly seen in the pulse radiolysis and laser photolysis experiments described in Section 1.

b) The reaction of $SO_4^{\bullet-}$ with benzyl alcohol. Deoxygenated aqueous solutions containing 1 mM benzyl alcohol, 1 mM $K_2S_2O_8$ [to yield $SO_4^{\bullet-}$, eqn. (5)], 0.2 M *tert*-butyl alcohol (to scavenge $OH^{\bullet}$), 2 mM $K_3Fe(CN)_6$ (to oxidize any hydroxy-cyclohexadienyl radicals formed), and 1 mM phosphate at pH 6 were γ-irradiated with doses such that conversion remained <10%. The products were identified (using GC and HPLC with optical and electrochemical detection) as the isomeric hydroxy-benzyl alcohols, benzaldehyde and a small amount of phenol, *i.e.* the same products as in the case of the $^{\bullet}OH$ reaction (see Table 3). However, the distribution of the products is different; specifically, there is much more benzaldehyde, showing that the α-hydroxybenzyl radical is formed in much higher yield than in the case of the $^{\bullet}OH$ reaction.

The results are explained by Scheme 2, in which it is assumed[48] that the $SO_4^{\bullet-}$ radical reacts with benzyl alcohol by electron transfer[49] to give a radical cation–SO_4^{2-} ion pair which reacts further *via* two channels: a) nucleophilic addition of water to the radical cation ("hydration") at all ring positions including *ipso* (total yield 56%) followed by deprotonation from OH and b) deprotonation of one of benzylic H's (42%). As shown in section 2a, the "hydration" reaction is reversible, whereas the deprotonation from the benzylic carbon is not. Addition and deprotonation are approximately equally fast, a situation quite different from the case of the toluene radical cation, which shows a pronounced preference for addition of water rather than C–H deprotonation.[19,27,28,30,31,50] The higher tendency to deprotonate is probably the result of a higher acidity of the benzyl carbon in the case of its substitution by
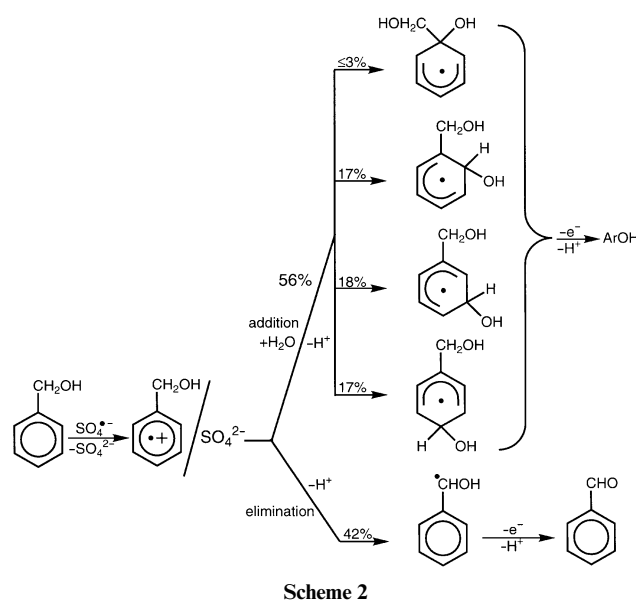
Scheme 2

the electron-seeking OH group. Stabilization of the incipient radical by the α-OH group, as recently suggested,[51] goes in the same direction.

Also, the *ortho*-, *meta*-, *para*-isomer ratio is different from that in the case of addition of $^{\bullet}OH$ to the ring. Addition of H_2O to the *para*-carbon of the radical cation is *twice* as likely as that to an *ortho*- or *meta*-position, compared to a factor of only ~1.5 in the case of $^{\bullet}OH$ addition to the benzyl alcohol parent.

The question as to what extent the radical cation is "free", *i.e.* uninfluenced by the counter-ion SO_4^{2-}, will be addressed below.

c) Products from the 248 nm laser photolysis of benzyl alcohol. Samples (3 mL) of deoxygenated aqueous solutions containing 10 mM benzyl alcohol and 1–2 mM $Fe^{III}(CN)_6^{3-}$ in 1 × 1 cm quartz cuvettes were photolyzed with the unfocused 248 nm light (KrF*) of the Lambdaphysik 103 EMG ESC excimer laser, using 200 to 2000 "shots". The power per pulse ("shot") was typically 150 mJ. The irradiated samples were subjected to HPLC analysis, using the same conditions as described in sections a, b. With $\leq$400 shots, the conversion was $\leq$1%, and the main photolysis products were the isomeric hydroxybenzyl alcohols and benzaldehyde. Additional products were seen but were not identified.[52] The distribution of products identified is presented in row 3 of Table 3.

d) Mechanistic conclusions. From these data it is evident that the ratio of ring addition products (the phenols) to benzaldehyde (derived from oxidation of the side chain) is not very

different from that in the case of the reaction of $SO_4^{\cdot-}$. However, there is a large difference with respect to the ratio of the isomers of hydroxybenzyl alcohols, the *para*-position being much more favored in the case of 248 nm photolysis than in the case of reaction of $SO_4^{\cdot-}$. The conclusion is thus that the species formed by $SO_4^{\cdot-}$ reaction and by photolysis are not the same. The ion pair produced by electron removal by $SO_4^{\cdot-}$ [radical cation–SO_4^{2-}][53,54] should have a reactivity different from the [radical cation–electron] pair. The latter is a "special" ion pair, due to the very rapid (300 fs [55,56]) solvation of the electron,[57] by which the bulky and only weakly solvated radical cation is left behind "naked". Since in water (even "conventional") ion pairs are typically very short-lived ($\leq$20 ps)[53,57] the addition of water to the one-electron-oxidized aromatic ring in the ion pair must take place on a similarly short time scale in order to compete with the ion-pair separation (= formation of free ions). This implies a very high electrophilic/deprotonation reactivity ($k_{1.o.} \geq 5 \times 10^{10}$ s^{-1}) of the benzyl alcohol radical cation in the [radical cation–SO_4^{2-}] pair.

Experimental

The benzyl alcohols and ether(s) were from commercial sources and they were fractionally distilled to a purity $\geq$99.8%. Water was from a Millipore system, acetonitrile was of spectroscopic grade. The solutions, after removing air by bubbling with argon, were pumped through the 2 by 4 mm Suprasil quartz cell (flow rates *ca.* 0.2–0.5 mL min^{-1}) and photolyzed with unfocused 20 ns pulses of 248 nm light (total energy *ca.* 5–40 mJ per pulse) from a Lambda-Physik EMG ESC excimer laser. The light-induced optical transmission changes were digitized by Tektronix 7612 and 7912 transient recorders interfaced with a DEC LSI11/73$^+$ computer which also process-controlled the apparatus and on-line preanalyzed the data. Final data analysis was performed on a Microvax I connected to the LSI. The error in the quantum yields and extinction coefficients is estimated as $\pm$10%.

For identification of photo- or radiation-chemical products (the conversion was always $\leq$1%), a ~1 mM solution of the substrates in aqueous solution in the absence or presence of additives such as $K_2S_2O_8$ or *tert*-butyl alcohol (the latter to scavenge radiation-chemically produced $\cdot$OH) was photolyzed (in a 1 cm quartz cuvette) or γ-irradiated (after saturation of the solution with N_2O) and analyzed by HPLC, using a 150 × 4.6 mm Luna-5-C_{18} column (from Phenomenex) with 0.8 mL min^{-1} MeOH–H_2O 1:2 as eluent (containing 0.01 M $NaClO_4$ in the case of electrochemical detection) and optical (Shimadzu SPD-M6A diode array detector) and electrochemical (Perkin-Elmer LC 17, electrode potential 0.8 V) detection. Identification and quantitation of the photo- or radiation products was by comparison with authentic samples.

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