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Primary radicals in the photo-oxidation of aromatics — reactions of xylenols with $\cdot\text{OH}$, $\text{N}_3\cdot$ and $\text{H}\cdot$ radicals and formation and characterization of dimethylphenoxy, dihydroxydimethylcyclohexadienyl and hydroxydimethylcyclohexadienyl radicals by pulse radiolysis

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Abstract

Photo-oxidations of environmental organics in illuminated TiO_2 dispersions have implicated surface-bound $\cdot\text{OH}$ radicals and/or valence band holes. To explore the implications of the former oxidizing entity, six isomeric xylenols (dimethylphenols) were examined by pulsed (nanoseconds to milliseconds) radiolysis methods. The spectral and kinetic characteristics of formation and decay of the transients formed by the reaction of $\text{N}_3\cdot$, $\cdot\text{OH}$ and $\text{H}\cdot$ radicals with these xylenols were assessed in buffered (pH 4, 10^{-3} M phosphate) aqueous media, where the xylenols exist in their protonated form ($\text{p}K_a \approx 10.19\text{--}10.65$). The products from the reaction of $\text{N}_3\cdot$ with 2,6- and 3,4-xyleneol were exclusively the corresponding dimethylphenoxy radicals, formed via electron transfer followed by deprotonation. In contrast, except with 3,4-xyleneol, the principal radical intermediates formed initially upon reaction with $\cdot\text{OH}$ were the corresponding $\cdot\text{OH}$ adducts, the dihydroxydimethylcyclohexadienyl radicals. 3,4-Xyleneol was examined in the pH range 4–10. At $\text{pH} \leq 8$ the initial $\cdot\text{OH}$ adduct (dihydroxy-3,4-dimethylcyclohexadienyl radical) was subsequently transformed (about 20%–40%) via water elimination into the dimethylphenoxy radical. In contrast, at pH 9 and 10 the $\cdot\text{OH}$ adduct and the dimethylphenoxy radical were formed concurrently (about 60% $\cdot\text{OH}$ adduct and about 40% dimethylphenoxy species), the latter through an inner-sphere electron transfer pathway. The switch in behaviour from pH 8 to pH 9 suggests that the $\text{p}K_a$ of the dihydroxy-3,4-dimethylcyclohexadienyl radical is about 8–9, about 2 pK units below the $\text{p}K_a$ of the parent substrate (10.4). A mechanism for the conversion of the $\cdot\text{OH}$ adduct to the dimethylphenoxy radical is proposed. Reaction of 2,6-xyleneol with $\text{H}\cdot$ radicals gave exclusively the $\text{H}\cdot$ adduct (hydroxycyclohexadienyl radical), whose spectral characteristics are similar to those of the related $\cdot\text{OH}$ adduct.

Keywords: Photo-oxidation; Primary radicals; Pulse radiolysis; Xylenols

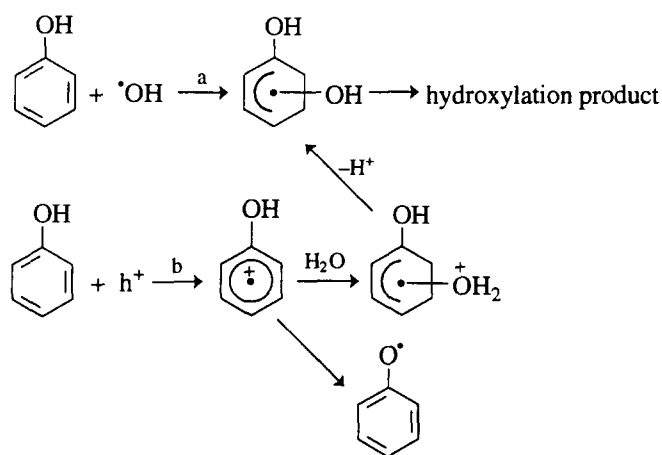
1. Introduction

The photocatalysed oxidation of methylated phenols in aqueous dispersions of TiO_2 has been demonstrated [1–3]. The compounds examined include *o*-, *m*- and *p*-cresol [1], the six isomers of dimethylphenol (hereafter referred to as xylenols) [2] and 2,3,5-trimethylphenol [3]. The hydroxyl radical has often been implicated as a significant if not the primary oxidant in TiO_2 -assisted photomineralizations of these and many other organic compounds in aqueous environments [4–9], since hydroxylated intermediates were detected during the photodegradation of several of these species.

In heterogeneous photocatalysis, two mechanisms have traditionally been proposed in the photo-oxidation of organic substrates in aqueous TiO_2 dispersions. The *first mechanism* postulates that the photogenerated valence band holes react primarily with physisorbed H_2O and surface-bound OH^- on TiO_2 particles (Eqs. (1) and (2)) to produce surface-bound $\cdot\text{OH}$ radicals which may subsequently react with preadsorbed or photoadsorbed organic substrates. The *second pathway* proposes a direct reaction between the valence band holes and the organic substrates.



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Scheme.

The two mechanisms cannot be differentiated by product analysis alone, since both pathways (Scheme, paths a and b) lead to the same products. Taking phenol as a representative environmental aromatic pollutant, $\cdot\text{OH}$ addition to the aromatic ring would yield the dihydroxycyclohexadienyl radical (path a) and subsequently such hydroxylated products [9] as hydroquinone, catechol and others. Direct hole oxidation of phenol (path b) would produce a radical cation which could, in principle, deprotonate to give the phenoxyl radical or could also hydrate to produce the dihydroxycyclohexadienyl radical and ultimately the same hydroxylated products [10,11]. The phenoxyl radical alone may turn out to be a dead-end in so far as the production of hydroxylated species is concerned [12].

A number of studies in the literature report on rates and mechanisms of $\cdot\text{OH}$ and other radical reactions with cresols [13–16]. No such studies have been reported for the xylenols.

The principal focus of the present study was to identify the primary radical products and assess the rates of reaction of such oxidizing radicals as $\cdot\text{OH}$ and $\text{N}_3\cdot$ and the reducing radical $\text{H}\cdot$ with the isomeric xylenols. The work was also aimed at establishing whether addition of $\cdot\text{OH}$ to the aromatic ring to give hydroxycyclohexadienyl species is a principal reaction pathway as present evidence would suggest [17–19], or the phenoxyl radical or both simultaneously. These studies were also needed to aid in identifying the primary oxidized species from (surface-bound) $\cdot\text{OH}$ radical attack on these xylenols, whose photomineralization over TiO_2 aqueous dispersions has been described earlier [2].

Herein we report on the identity, spectral properties and kinetics of formation and decay of radicals produced by the reaction of $\cdot\text{OH}$, $\text{N}_3\cdot$ and $\text{H}\cdot$ with these xylenols in homogeneous aqueous phase.

2. Experimental details

2.1. Chemicals

2,3-Xylenol (99%), 2,4-xylenol (97%), 2,5-xylenol (99+%), 2,6-xylenol (99.8+%), 3,4-xylenol (99%) and

3,5-xylenol (99+%; Aldrich) were used as received. Nitrogen and nitrous oxide (prepurified, Linde) were used as received. Sodium azide, potassium phosphate (MCB), potassium thiocyanate, *t*-butanol (Fisher Scientific) and other chemicals were reagent grade and were used as received. Millipore filtered water was used for all solutions.

2.2. Solutions

Hydroxyl radicals were generated in buffered (pH 4, 10^{-3} M phosphate buffer) aqueous solutions of xylenol except during the pH dependence study. The six xylenols examined in this work exist in their protonated form at pH 4; p*K*s range from 10.19 for 2,6-xylenol to 10.65 for 2,5-xylenol [10].

Deoxygenation was accomplished by bubbling the solution with N_2O . Azide radicals were generated in aqueous solutions of NaN_3 (0.01 M). The pH of the N_2O -purged sodium azide solution was adjusted to 5.8 to compare the values obtained for the rate constants with the corresponding values from the literature. Hydrogen atoms were generated in buffered (pH 1) aqueous solutions of xylenol containing 0.2 M *t*-butanol. In this case oxygen was removed by purging the solution with nitrogen.

Solutions ($20 \pm 2^\circ\text{C}$) were irradiated in a single-pass flow cell with a 2.5 cm analysing path length, with fresh sample being injected into the cell after each pulse. The concentrations of solutes were also chosen to ensure 90%–100% capture of the desired primary radicals. Additional details of the experimental conditions are summarized in the tables and figure captions.

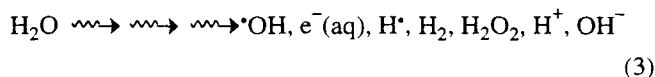
2.3. Pulse radiolysis experiments

2.3.1. Electron accelerator

Pulse radiolysis experiments were performed using a high voltage Engineering Corporation Van de Graaff accelerator (4 MeV, 1–3 A). The instrument had been modified to produce a pulsed beam of electrons with pulse durations of 50, 100, 250 and 500 ns [21]. The kinetic spectrometry apparatus consisted of a xenon lamp (450 W), a grating monochromator and a photomultiplier tube (Hamamatsu Corp. R928, multi-alkali cathode) arrangement, with all optical elements confined to a 1.5 m optical bench centred beneath the exit window of the vertically mounted accelerator. A fast shutter located between the sample and the lamp housing protected the sample from continuous photolysis by the analysing light; this shutter was opened only for a few microseconds during data collection. The electrical signal produced in the detector circuit by changes in the optical absorption in the target medium following an electron pulse was converted to intensity vs. time coordinates using a Lacroix 8818 digitizer interfaced with an IBM-compatible 386 computer. The radiation dose was measured with an energy meter; the readings were converted to radical concentrations using dosimetry.

2.3.2. Radical production and dosimetry

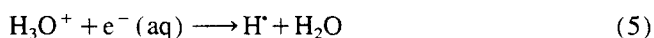
Radiolysis of water by high energy electrons produces various radical and molecular species (Eq. (3)) [22].



Hydroxyl radicals, hydrated electrons and hydrogen atoms are highly reactive species that can react with organic compounds to produce organic free radicals. To obtain the $\cdot\text{OH}$ radical as the primary radical, aqueous solutions were saturated with nitrous oxide ($[\text{N}_2\text{O}] = 25 \text{ mM}$) to ensure scavenging of the other highly reactive species. In addition to eliminating molecular oxygen, N_2O converts $\text{e}^-(\text{aq})$ to $\cdot\text{OH}$ (Eq. (4)). The quantity of H^\cdot atoms produced was controlled by varying the pH of the solution; the quantity of H^\cdot radicals produced at $\text{pH} > 3$ via Eq. (5) is negligible (less than 10% of radicals produced [23,24]).

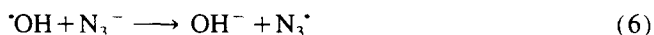


$$k = 9.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$



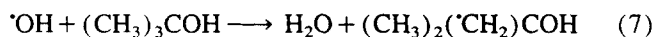
$$k = 2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$

The less reactive oxidizing azide radical (N_3^\cdot) was produced by reaction of $\cdot\text{OH}$ with NaN_3 (Eq. (6)); they are highly selective oxidizing agents and normally react with aromatic compounds via electron transfer, unlike $\cdot\text{OH}$ radicals where addition to the ring is usually the predominant path [13].



$$k = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$

Aqueous solutions of *t*-butanol provided a medium in which either H^\cdot or $\text{e}^-(\text{aq})$, depending on pH, was used as the principal radical to react with organic substrates, since *t*-butanol scavenges $\cdot\text{OH}$ radicals to give a relatively inert alkyl radical (Eq. (7)). Note that reactions of H^\cdot and $\text{e}^-(\text{aq})$ with *t*-butanol are slow: $k = 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ [23] and $4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ [25] respectively.



$$k = 6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

The absorbed radiation dose, and therefore the amount of a given radical in solution, was determined by thiocyanate dosimetry using 0.01 M KSCN in N_2O -saturated water.

3. Results and discussion: reactions of xlenols with various radical species

Reactions of xlenols with a variety of radical species ($\cdot\text{OH}$, N_3^\cdot and H^\cdot) have been examined by observing the changes in the optical density (OD) of the reaction medium.

The desired radical species were generated radiolytically in solution by varying the composition of the solution and the purging gases used (see Section 2).

3.1. Reaction with N_3^\cdot radicals

Because of our recent work on the pentahalophenols [26], it was relevant to assess the spectral properties of the phenoxyl radicals produced by the interaction of the xlenols with azide radicals, as the data were needed to differentiate spectrally between a phenoxyl radical and an $\cdot\text{OH}$ adduct. For this purpose, two xlenols were chosen after a preliminary study: 2,6-xylenol and 3,4-xylenol.

The absorption spectrum (Fig. 1a) of the product resulting from the oxidation of 2,6-xylenol by N_3^\cdot , the 2,6-dimethylphenoxyl radical, shows two absorption maxima: bands at 390 nm ($\epsilon_{390} = 3150 \pm 150 \text{ M}^{-1} \text{ cm}^{-1}$) and 375 nm ($\epsilon_{375} = 2950 \pm 300 \text{ M}^{-1} \text{ cm}^{-1}$).

The oxidation of 2,6-xylenol by N_3^\cdot (Eq. (8)) was monitored at 375 nm by following the increase in optical density

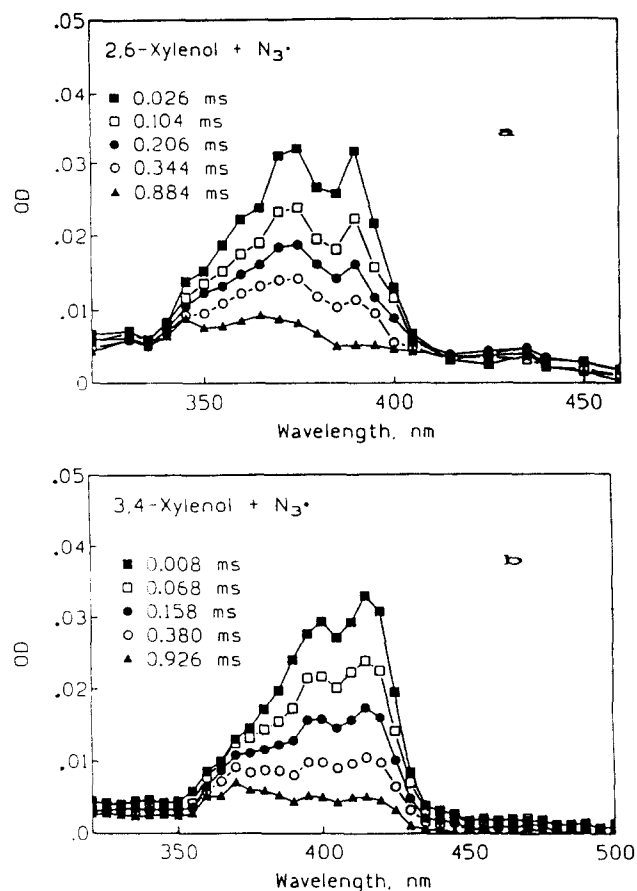


Fig. 1. (a) Transient absorption spectra of the 2,6-dimethylphenoxyl radical at 0.026, 0.104, 0.206, 0.344 and 0.884 ms following irradiation of $3.0 \times 10^{-4} \text{ M}$ 2,6-xylenol at pH 5.8 in a 0.01 M NaN_3 aqueous solution. The solution was N_2O saturated; $[\cdot\text{OH}] = 5.20 \times 10^{-6} \text{ M}$. (b) Transient absorption spectra of the 3,4-dimethylphenoxyl radical at 0.008, 0.068, 0.158, 0.380 and 0.926 ms following irradiation of $3.0 \times 10^{-4} \text{ M}$ 3,4-xylenol at pH 5.8 in a 0.01 M NaN_3 aqueous solution. The solution was N_2O saturated; $[\cdot\text{OH}] = 4.78 \times 10^{-6} \text{ M}$.

Table 1
Observed kinetics of formation and decay of phenoxyl radicals in various reaction systems ^a

Reaction system	Formation		Decay	
	λ (nm) ^b	$10^{-5} k_{\text{obs}}$ (s ⁻¹)	λ (nm) ^b	$10^{-5} k_{\text{obs}}$ (s ⁻¹) ^c
2,6-Xylenol + N ₃ ⁻ + [•] OH	375 ^d	2.7-8.1	375 ^e	5.1 ± 0.3
			390 ^e	5.2 ± 0.3
3,4-Xylenol + N ₃ ⁻ + [•] OH	415 ^f	2.7-8.1	400 ^g	2.2 ± 0.3
			415 ^g	1.9 ± 0.2

^a General conditions: N₂O-saturated solutions (25 mM); pH 5.8; [NaN₃] = 0.01 M.

^b Monitoring wavelength.

^c Equivalent to k/el (see text for meaning).

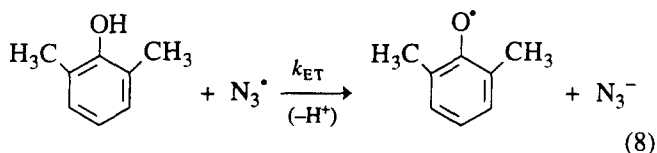
^d [2,6-Xylenol] = (1.0-3.0) × 10⁻⁴ M; [[•]OH] = 3.34 × 10⁻⁶ M.

^e [2,6-Xylenol] = 3.0 × 10⁻⁴ M; [[•]OH] = (3.0-10) × 10⁻⁶ M.

^f [3,4-Xylenol] = (0.5-3.0) × 10⁻⁴ M; [[•]OH] = 1.68 × 10⁻⁶ M.

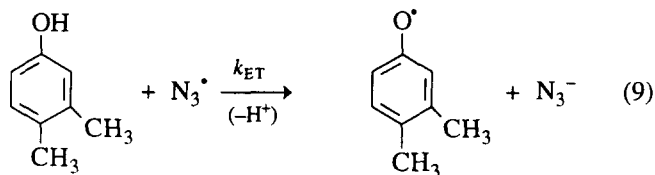
^g [3,4-Xylenol] = 3.0 × 10⁻⁴ M; [[•]OH] = (1.0-7.0) × 10⁻⁶ M.

with changes in the 2,6-xylenol concentration from 1.0 × 10⁻⁴ to 3.0 × 10⁻⁴ M; the electron transfer rate constant k_{ET} is (2.8 ± 0.6) × 10⁹ M⁻¹ s⁻¹ (Table 1). The transient with absorptions at either 375 or 390 nm decayed via second-order kinetics: $k_d = (4.2 ± 0.9) × 10^9$ M⁻¹ s⁻¹. The kinetics of formation and decay of the 2,6-dimethylphenoxyl radical and its spectral properties accord with those of similar compounds (Table 1) [13,14,27].



The reaction of 3,4-xylenol with N₃[•] gave the corresponding 3,4-dimethylphenoxyl radical, whose spectrum (Fig. 1b) is also characterized by two bands at 400 nm ($\epsilon_{400} = 2900 ± 300$ M⁻¹ cm⁻¹) and 415 nm ($\epsilon_{415} = 3300 ± 500$ M⁻¹ cm⁻¹). The oxidation of 3,4-xylenol (Eq. (9)) was moni-

tored at the latter wavelength via the temporal increase in optical density vs. [3,4-xylenol] over the range 5.0 × 10⁻⁵–3.0 × 10⁻⁴ M; from the observed rate constant k_{obs} (Table 1), $k_{\text{ET}} = (4.1 ± 0.6) × 10^9$ M⁻¹ s⁻¹ for the oxidation. The transient decay at 400 and 415 nm followed second-order kinetics: $k_d = (1.5 ± 0.3) × 10^9$ M⁻¹ s⁻¹. The kinetics of formation and decay together with the spectral properties of the 3,4-dimethylphenoxyl radical correlate well with those of similar compounds (Table 1) [13,14,27].



3.2. Reaction with [•]OH radicals

3.2.1. Dihydroxydimethylcyclohexadienyl radicals

Hydroxyl radicals typically add to phenols (e.g. phenol [14], cresol [14], 2,4,5-trichlorophenol [19]) to form dihydroxycyclohexadienyl radicals ([•]OH adducts), in competition with hydrogen atom abstraction and electron transfer [13]. Phenoxyl radicals can also form from the [•]OH adduct either via electron transfer or via unimolecular elimination of H₂O [14].

The absorption spectrum of the adduct produced by the reaction of [•]OH with 2,6-xylenol, illustrated in Fig. 2, shows an absorption maximum at about 320 nm ($\epsilon_{320} = 2700 ± 300$ M⁻¹ cm⁻¹). The intermediate decayed via second-order kinetics (k/el , Table 2): $k_d = (4.1 ± 0.9) × 10^9$ M⁻¹ s⁻¹.

The rate constant for the addition of [•]OH to 2,6-xylenol was measured at various concentrations of 2,6-xylenol: $k_{\text{obs}} = (1.5-3.2) × 10^6$ s⁻¹ (Table 2), yielding $k_{\text{add}} = (1.2 ± 0.2) × 10^{10}$ M⁻¹ s⁻¹ for reaction (10). The kinetics of formation and decay of the intermediate radical as well as its spectral properties conform with those of similar hydroxycyclohexadienyl radicals reported earlier (Table 3) and con-

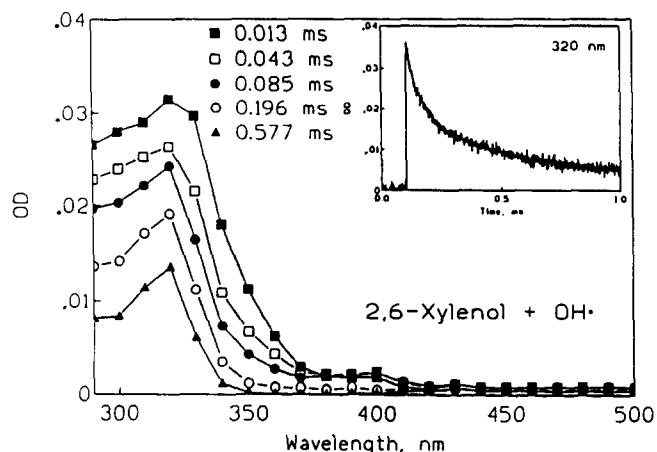


Fig. 2. Transient absorption spectra of the dihydroxy-2,6-dimethylcyclohexadienyl radical monitored at 0.013, 0.043, 0.085, 0.196 and 0.577 ms following irradiation of a 2.5 × 10⁻⁴ M aqueous 2,6-xylenol solution buffered at pH 4. The solution was N₂O saturated; [[•]OH] = 5.02 × 10⁻⁶ M. The inset shows the decay of the optical density at 320 nm.

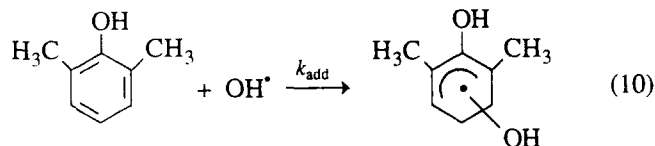
Table 2

Observed kinetics of formation and decay of OH adducts of xylenols in various reaction systems ^a

Reaction system	Formation		Decay	
	λ (nm)	k_{obs} (s^{-1})	λ (nm)	k_{obs} ($k/\epsilon l$) (s^{-1})
2,3-Xylenol + $\cdot\text{OH}$	300 ^b	$(9.8\text{--}27) \times 10^5$	300 ^c	$(7 \pm 2) \times 10^4$
2,4-Xylenol + $\cdot\text{OH}$	300 ^d	$(8.4\text{--}24) \times 10^5$	300 ^c	$(1.4 \pm 0.2) \times 10^5$
2,5-Xylenol + $\cdot\text{OH}$	330 ^f	$(1.0\text{--}3.3) \times 10^6$	330 ^g	$(3.9 \pm 0.8) \times 10^5$
2,6-Xylenol + $\cdot\text{OH}$	320 ^h	$(1.5\text{--}3.2) \times 10^6$	320 ⁱ	$(6.1 \pm 1.2) \times 10^5$
3,5-Xylenol + $\cdot\text{OH}$	310 ^j	$(1.1\text{--}2.9) \times 10^6$	310 ^k	$(3.4 \pm 0.7) \times 10^5$

^a General conditions: N_2O -saturated solutions (25 mM); pH 4 (10^{-3} M phosphate buffer).^b [2,3-Xylenol] = $(1.0\text{--}2.5) \times 10^{-4}$ M; [$\cdot\text{OH}$] = 2.5×10^{-6} M.^c [2,3-Xylenol] = 2.5×10^{-4} M; [$\cdot\text{OH}$] = $(2.3\text{--}9.0) \times 10^{-6}$ M.^d [2,4-Xylenol] = $(1.0\text{--}2.5) \times 10^{-4}$ M; [$\cdot\text{OH}$] = 2.69×10^{-6} M.^e [2,4-Xylenol] = 2.5×10^{-4} M; [$\cdot\text{OH}$] = $(3.0\text{--}10) \times 10^{-6}$ M.^f [2,5-Xylenol] = $(1.0\text{--}3.0) \times 10^{-4}$ M; [$\cdot\text{OH}$] = 3.0×10^{-6} M.^g [2,5-Xylenol] = 3.0×10^{-4} M; [$\cdot\text{OH}$] = $(2.8\text{--}10) \times 10^{-6}$ M.^h [2,6-Xylenol] = $(1.0\text{--}2.5) \times 10^{-4}$ M; [$\cdot\text{OH}$] = 4.22×10^{-6} M.ⁱ [2,6-Xylenol] = 2.5×10^{-4} M; [$\cdot\text{OH}$] = $(3.0\text{--}10) \times 10^{-6}$ M.^j [3,5-Xylenol] = $(1.0\text{--}3.0) \times 10^{-4}$ M; [$\cdot\text{OH}$] = 2.8×10^{-6} M.^k [3,5-Xylenol] = 3.0×10^{-4} M; [$\cdot\text{OH}$] = $(2.0\text{--}9.0) \times 10^{-6}$ M.

firm its identity as the dihydroxy-2,6-dimethylcyclohexadienyl radical.



Reactions of the related 2,3-, 2,4-, 2,5- and 3,5-xylenol with $\cdot\text{OH}$ showed a behaviour similar to that of 2,6-xylenol and produced only the corresponding $\cdot\text{OH}$ adducts. The experimental conditions and observations are summarized in Table 2 and the spectral and kinetic properties of the radicals produced are summarized in Table 3. The time-resolved absorption spectra for the relevant $\cdot\text{OH}$ radical adducts are depicted in Fig. 3. The reaction between $\cdot\text{OH}$ and 3,4-xylenol produced a different product distribution (see below).

Rate constants for $\cdot\text{OH}$ addition to xylenols in the gas phase [28] are compared with the values obtained in aqueous solution in Table 4. Both sets of values are within the same order of magnitude, although the rate constants in the gas phase are generally larger by a factor of about 4–6. This is not surprising, as both sets of data are controlled by diffusion rates of the molecules, which must be faster in the gas phase than in solution.

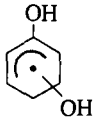
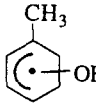
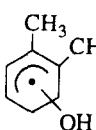
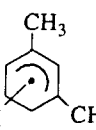
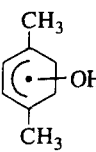
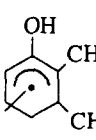
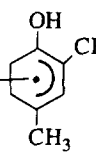
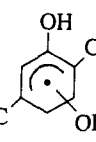
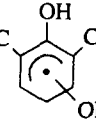
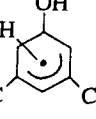
Benzylic radicals are formed in alkaline solutions by reacting $\text{O}^{\cdot -}$ (deprotonated form of $\cdot\text{OH}$) with methylated benzenes via abstraction of a hydrogen atom from a benzylic methyl group [30]. These radicals can also form in acidic media via water elimination from $\cdot\text{OH}$ radical adducts. Absorption spectra of benzyl radicals formed from methylated benzenes are typically characterized by three absorption bands, one at 260–270 nm ($\epsilon = 15\,000\text{ M}^{-1}\text{ cm}^{-1}$) and two in the 300–330 nm region ($\epsilon \approx 3000\text{--}5000\text{ M}^{-1}\text{ cm}^{-1}$). Methylated benzyl radicals normally decay via second-order

kinetics with $k \approx 2.0 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ [28]; they are formed, however, at slower rates than the $\cdot\text{OH}$ adducts (e.g. for toluene the rate constant for H atom abstraction is $k_{\text{abs}} = 4.0 \times 10^8\text{ M}^{-1}\text{ s}^{-1}$ and the rate constant for $\cdot\text{OH}$ adduct formation is $k_{\text{add}} = 6.8 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ [29]). The percentages of hydrogen atom abstraction products from mono- and dimethylbenzenes by reaction with $\cdot\text{OH}$ range from 6% to 12% in alkaline solution, with the $\cdot\text{OH}$ adduct comprising the remaining fraction [29]. Our present data do not preclude the likelihood that some hydrogen atom abstraction products may have formed. However, kinetic and spectral data, under the experimental conditions used (acidic pH), favour the $\cdot\text{OH}$ adduct as the initial product. An alternative reaction pathway for the $\cdot\text{OH}$ adducts is the elimination of H_2O to give phenoxyl radicals owing to the presence of an OH group on the ring in addition to the methyl groups. Phenoxyl radicals are detectable under our experimental conditions.

3.2.2. Reaction of 3,4-xylenol with $\cdot\text{OH}$ radicals

The absorption spectrum of the product(s) of the reaction of $\cdot\text{OH}$ with 3,4-xylenol is somewhat unique; it is depicted in Fig. 4. The spectrum was recorded under conditions similar to those used for the other five isomers of xylenol (Figs. 2 and 3). It shows one band with an absorption maximum at 300 nm and a shoulder between 400 and 420 nm. The transient absorbing at 300 nm decayed via second-order kinetics: $k/\epsilon l = (1.9 \pm 0.3) \times 10^5\text{ s}^{-1}$. The absorption band at 400–420 nm built up at a visibly slower rate ($k_{\text{obs}} \approx 10^4\text{ s}^{-1}$) and decayed by second-order kinetics ($k/\epsilon l \approx 2 \times 10^5\text{ s}^{-1}$ at 415 nm). This suggests that the two bands originate from different species. The similarity of the decay constant at 415 nm (see above) to the second-order decay constant of the 3,4-dimethylphenoxyl radical at 415 nm (Fig. 1b, $k/\epsilon l = (1.9 \pm 0.2) \times 10^5\text{ s}^{-1}$) indicates that the 3,4-dimethyl-

Table 3
Comparison of optical and kinetic properties of dihydroxydimethylcyclohexadienyl radicals with values published for similar radicals

Radical	λ_{\max} (nm)	ϵ_{\max} ($M^{-1} \text{ cm}^{-1}$)	k_f ($M^{-1} \text{ s}^{-1}$)	k_d ($M^{-1} \text{ s}^{-1}$)	Ref.
	330	4400	1.4×10^{10}	3.6×10^9	[14]
	320	4300	6.8×10^9	1.6×10^9	[29]
	326	4700	6.7×10^9	1.4×10^9	[29]
	328	6000	7.5×10^9	1.3×10^9	[29]
	312	4300	7.0×10^9	1.2×10^9	[29]
	300	2900 ± 450	$(1.2 \pm 0.2) \times 10^{10}$	$(5.0 \pm 1.0) \times 10^8$	*
	300	3300 ± 500	$(1.0 \pm 0.2) \times 10^{10}$	$(1.2 \pm 0.3) \times 10^9$	*
	330	3000 ± 300	$(1.0 \pm 0.2) \times 10^{10}$	$(2.9 \pm 0.5) \times 10^9$	*
	320	2700 ± 300	$(1.2 \pm 0.2) \times 10^{10}$	$(4.1 \pm 0.9) \times 10^9$	*
	310	2800 ± 150	$(9.6 \pm 0.2) \times 10^9$	$(2.4 \pm 0.5) \times 10^9$	*

* This work.

phenoxy radical is formed in the reaction of 3,4-xylenol with $\cdot\text{OH}$ radicals.

Subtraction of the contribution of the 3,4-dimethylphenoxy radical absorption (open squares) from the 3,4-xylenol + $\cdot\text{OH}$ spectrum (full squares) gives the difference

spectrum indicated (full circles) in Fig. 5. We attribute this difference spectrum to the $\cdot\text{OH}$ radical adduct of 3,4-xylenol, i.e. to the dihydroxy-3,4-dimethylcyclohexadienyl radical, from its similarity to the spectra of $\cdot\text{OH}$ adducts of the other five xylenols (Fig. 2, Table 3, Fig. 3).

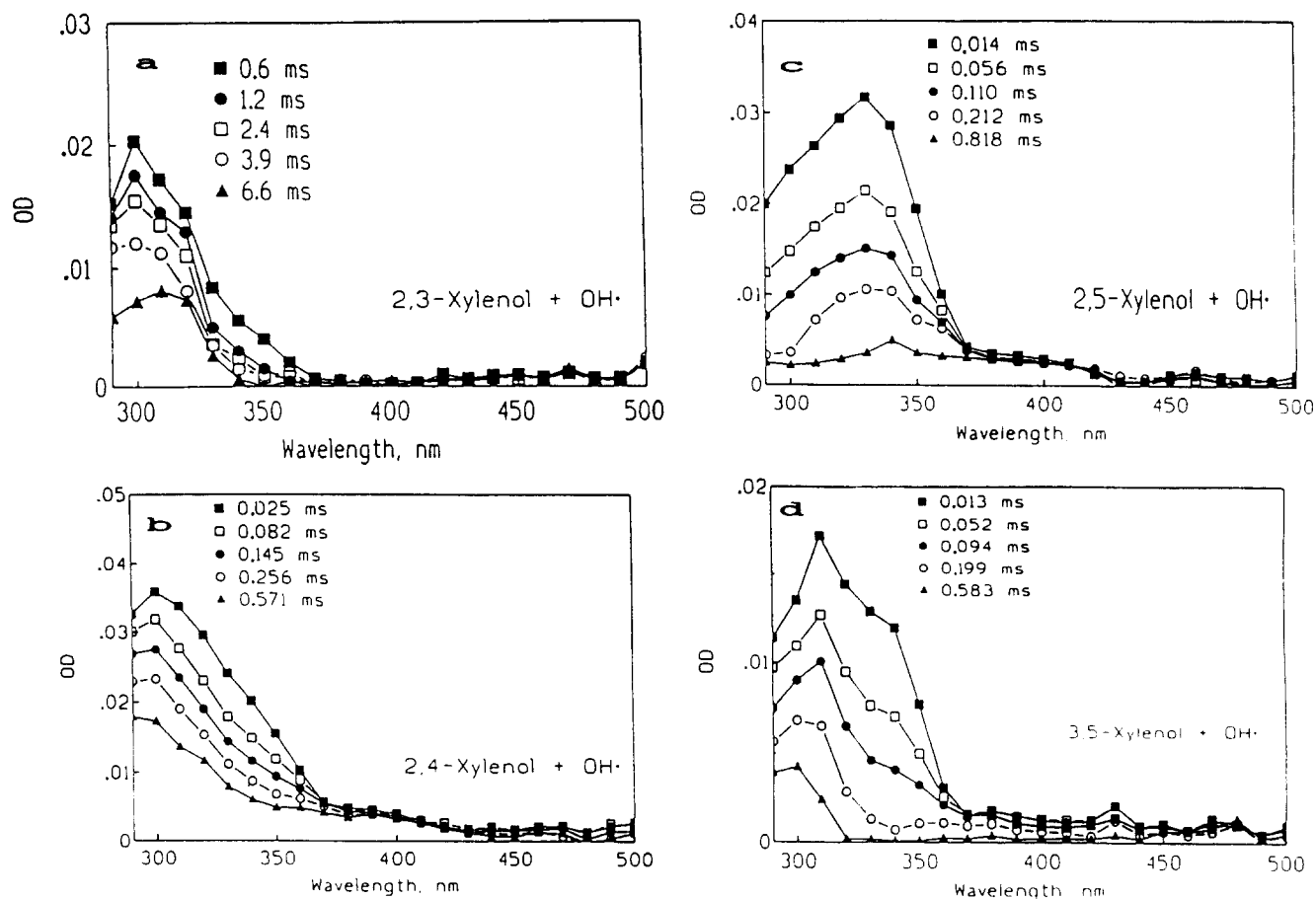


Fig. 3. (a) Transient absorption spectra of the reaction product between 2,3-xyleneol and $\cdot\text{OH}$ monitored at 0.6, 1.2, 2.4, 3.9 and 6.6 ms following irradiation of a 2.5×10^{-4} M aqueous 2,3-xyleneol solution buffered at pH 4 (see Section 2). The solution was N_2O saturated; $[\cdot\text{OH}] = 4.87 \times 10^{-6}$ M. (b) Transient absorption spectra of the reaction product between 2,4-xyleneol and $\cdot\text{OH}$ monitored at 0.025, 0.082, 0.145, 0.256 and 0.571 ms after irradiation of a 2.5×10^{-4} M aqueous 2,4-xyleneol solution buffered at pH 4 (see Section 2). The solution was N_2O saturated; $[\cdot\text{OH}] = 5.16 \times 10^{-6}$ M. (c) Transient absorption spectra of the reaction product between 2,5-xyleneol and $\cdot\text{OH}$ monitored at 0.014, 0.056, 0.110, 0.212 and 0.818 ms following irradiation of a 3.0×10^{-4} M aqueous 2,5-xyleneol solution buffered at pH 4 (see Section 2). The solution was N_2O saturated; $[\cdot\text{OH}] = 5.45 \times 10^{-6}$ M. (d) Transient absorption spectra of the reaction product between 3,5-xyleneol and $\cdot\text{OH}$ monitored at 0.013, 0.052, 0.094, 0.199 and 0.583 ms following irradiation of a 3.0×10^{-4} M aqueous 3,5-xyleneol solution buffered at pH 4 (see Section 2). The solution was N_2O saturated; $[\cdot\text{OH}] = 2.93 \times 10^{-6}$ M.

Table 4

Comparison of rates of $\cdot\text{OH}$ addition to xylenols in aqueous solution and in the gas phase

Xylenol	k_{add} ($\text{M}^{-1} \text{s}^{-1}$) (gas phase) ^a	k_{add} ($\text{M}^{-1} \text{s}^{-1}$) (aqueous solution) ^b
2,3-Xylenol	$(4.8 \pm 1.2) \times 10^{10}$	$(1.2 \pm 0.2) \times 10^{10}$
2,4-Xylenol	$(4.3 \pm 1.1) \times 10^{10}$	$(1.0 \pm 0.2) \times 10^{10}$
2,5-Xylenol	$(4.8 \pm 1.4) \times 10^{10}$	$(1.0 \pm 0.2) \times 10^{10}$
2,6-Xylenol	$(4.0 \pm 1.0) \times 10^{10}$	$(1.2 \pm 0.2) \times 10^9$
3,4-Xylenol	$(4.9 \pm 1.3) \times 10^{10}$	$(9.0 \pm 1.0) \times 10^9$ (see text)
3,5-Xylenol	$(6.8 \pm 1.8) \times 10^{10}$	$(9.6 \pm 0.2) \times 10^9$

^a From Ref. [28]. Values obtained at 296 K.

^b This work. Values obtained at 293 K.

The kinetic data were ambiguous on whether the 3,4-dimethylphenoxy radical was produced by unimolecular elimination of H_2O ($k/\epsilon l = (1.9 \pm 0.3) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for the disappearance of the $\cdot\text{OH}$ adduct; $k_{\text{obs}} \approx 10^4 \text{ s}^{-1}$ for the formation of the phenoxy radical). To establish the source of the phenoxy radical, the absorption spectrum of the products

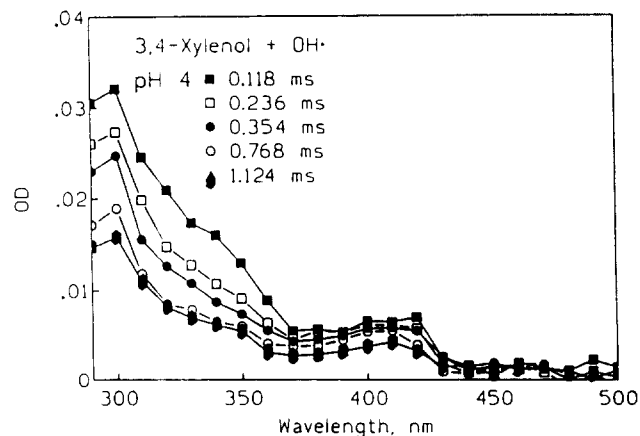


Fig. 4. Transient absorption spectra of the reaction product between 3,4-xyleneol and $\cdot\text{OH}$ monitored at 0.118, 0.236, 0.354, 0.768 and 1.124 ms following irradiation of a 3.0×10^{-4} M aqueous 3,4-xyleneol solution buffered at pH 4. The solution was N_2O saturated; $[\cdot\text{OH}] = 6.01 \times 10^{-6}$ M.

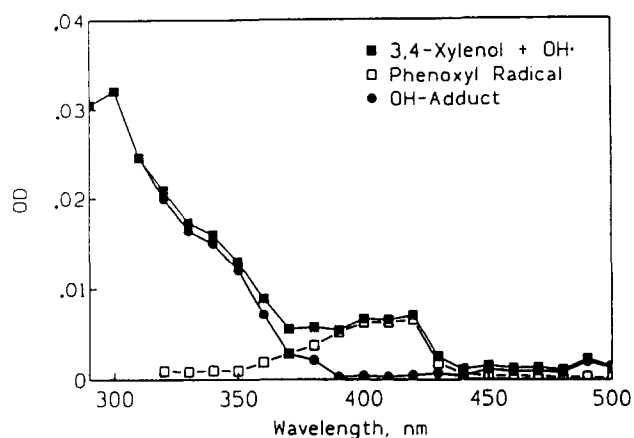


Fig. 5. Transient difference absorption spectrum of the dihydroxy-3,4-dimethylcyclohexadienyl radical (●) as calculated from the transient absorption spectrum of the products of the reaction between 3,4-xyleneol and $\cdot\text{OH}$ (■) at $118 \mu\text{s}$ following irradiation of a $2 \times 10^{-4} \text{ M}$ aqueous 3,4-xyleneol solution buffered at pH 4. The solution was N_2O saturated; $[\cdot\text{OH}] = 6.01 \times 10^{-6} \text{ M}$. The open squares (□) represent the contribution to the product spectrum of the 3,4-dimethylphenoxyl radical.

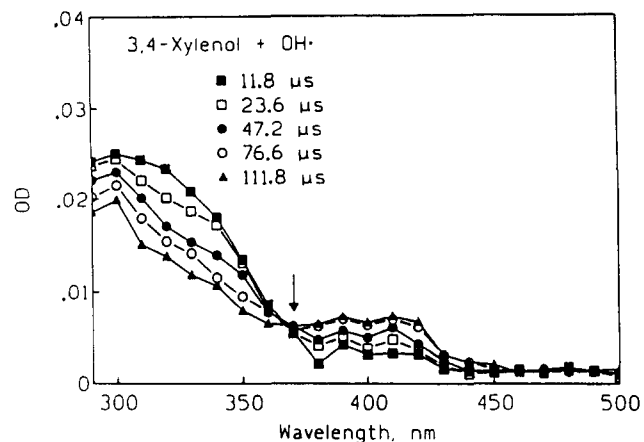


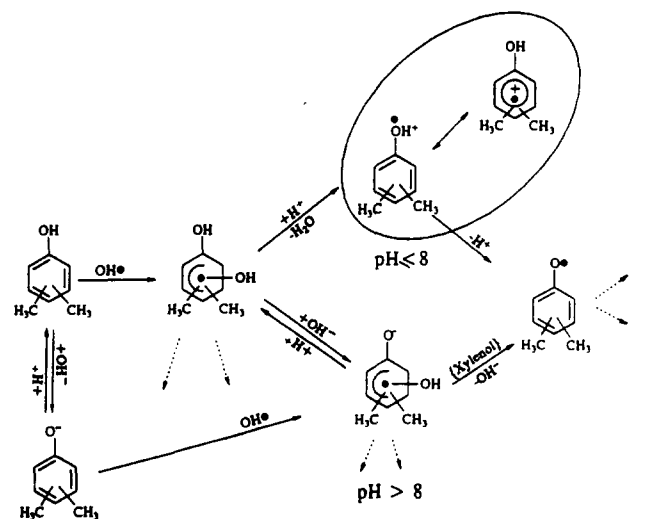
Fig. 6. Transient absorption spectra of the reaction product(s) between 3,4-xyleneol and $\cdot\text{OH}$ monitored at 11.8, 23.6, 47.2, 76.6 and $111.8 \mu\text{s}$ following irradiation of a $3.0 \times 10^{-4} \text{ M}$ aqueous 3,4-xyleneol solution buffered at pH 4. The solution was N_2O saturated; $[\cdot\text{OH}] = 2.99 \times 10^{-6} \text{ M}$.

of the reaction of $\cdot\text{OH}$ with 3,4-xyleneol was recorded on a shorter time scale (0–200 μs). The spectrum (Fig. 6) shows the simultaneous decrease in optical density of the 300 nm band and growth of the 400 nm band: a clean isosbestic point is clearly seen at about 370 nm. The shape of the band at 300 nm and the observed product distribution (about 24% $\cdot\text{OH}$ adduct converted to phenoxyl) infer that one isomer of the $\cdot\text{OH}$ adduct (probably that in which the $\cdot\text{OH}$ added to an ortho carbon) likely undergoes H_2O elimination to the corresponding phenoxyl radical. The major fraction of the $\cdot\text{OH}$ adduct decays by a bimolecular reaction; this is consistent with the observed kinetics (second order) for the decay of the transient at 300 nm.

3.2.3. Mechanism(s) of product radical formation

The rate of formation of the phenoxyl radical was independent of the initial concentration of 3,4-xyleneol in acid media (pH 4), consistent with the formation of phenoxyl

radicals via H_2O elimination. Our results infer the mechanism shown in Eq. (11) for the reaction of $\cdot\text{OH}$ radicals with 3,4-xyleneol at pH 4 to give the dihydroxy-3,4-dimethylcyclohexadienyl radical and subsequently the 3,4-dimethylphenoxyl radical [14]. The initially produced dihydroxy-cyclohexadienyl radical undergoes unimolecular dehydration to the corresponding phenoxyl radical. For phenol [14] the dehydration is catalysed by either acid or base, with the uncatalysed elimination rate being less than (or equal to) 10^3 s^{-1} . We saw no evidence for the formation of phenoxyl radicals from the other five isomers of xyleneol in the present study; their formation is not precluded if their quantity was too small to go undetected. Taking ϵ_{max} as about $3000 \text{ M}^{-1} \text{ cm}^{-1}$, $1.3 \times 10^{-6} \text{ M}$ of the phenoxyl radicals would have to form to give an absorbance change of 0.01. The mechanism depicted in Eq. (11) is therefore presumed to also apply, to a lesser degree, to the reactions of the other xyleneols examined.



(11)

Using the extinction coefficient at 300 nm of the dihydroxy-3,4-dimethylcyclohexadienyl radical obtained from $(\text{OD})_0$ at 300 nm (prior to phenoxyl formation; $\epsilon_{300} = 3000 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$) gives $k_d \approx 1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the second-order decay path. The first-order component that produces the phenoxyl radical (acid path in Eq. (11)) must be relatively unimportant, since the observed decay of the $\cdot\text{OH}$ adduct followed good second-order kinetics.

The kinetics of $\cdot\text{OH}$ addition to 3,4-xyleneol were determined at various concentrations of 3,4-xyleneol (1.0 – $4.0 \times 10^{-4} \text{ M}$): k_{obs} ranges from 1.0×10^6 to $3.8 \times 10^6 \text{ s}^{-1}$ ($\lambda = 300 \text{ nm}$) and gives a rate constant of $(9.0 \pm 1.0) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the addition step.

3.2.4. pH dependence of the reaction between $\cdot\text{OH}$ and 3,4-xyleneol

The reaction of 3,4-xyleneol with $\cdot\text{OH}$ radicals was also examined at various pHs. The pH range between 4 and 10 permitted minimal interference from H^+ radicals (pH ≤ 3) and $\text{O}^{\cdot-}$ radicals (pH ≥ 10) ($\text{p}K_a(\cdot\text{OH}) = 11.9$ [23]). The

Table 5

Data obtained from the pH dependence study of the reaction of 3,4-xyleneol with $\cdot\text{OH}$

3,4-Xyleneol + $\cdot\text{OH}$ (300 nm)		Phenoxy formation (415 nm)			
pH	k_f ($\text{M}^{-1} \text{s}^{-1}$) ^a	k_{obs} (s^{-1}) (fixed dose) ^b	Conversion to phenoxy (%)		
4 ^c	$(9.0 \pm 1.0) \times 10^9$	$(4.4 \pm 0.2) \times 10^4$	24 ^d		
5	–	–	19 ^e		
6 ^f	$(1.1 \pm 0.2) \times 10^{10}$	$(3.3 \pm 0.4) \times 10^4$	26 ^g		
7	–	–	39 ^h		
8 ⁱ	$(5.1 \pm 0.6) \times 10^9$	$(4.8 \pm 0.7) \times 10^4$	33 ^j		
pH	k_{obs} ($\text{M}^{-1} \text{s}^{-1}$) ^k	k_{add} ($\text{M}^{-1} \text{s}^{-1}$) ^l	k_{obs} ($\text{M}^{-1} \text{s}^{-1}$) ^k	k_{ET} ($\text{M}^{-1} \text{s}^{-1}$) ^m	Phenoxy in product (%)
9 ⁿ	$(5.6 \pm 0.5) \times 10^9$	3.2×10^9	$(5.4 \pm 0.6) \times 10^9$	2.3×10^9	42 ^o
10 ^p	$(5.1 \pm 0.6) \times 10^9$	3.2×10^9	$(5.3 \pm 0.5) \times 10^9$	2.0×10^9	38 ^q

^a Rate constant for the addition of $\cdot\text{OH}$ to 3,4-xyleneol as determined from a concentration dependence study.^b Observed rate constant at fixed $[\cdot\text{OH}]$.^c $[3,4\text{-Xyleneol}] = (1.0\text{--}4.0) \times 10^{-4} \text{ M}$; $k_{\text{obs}} = (1.0\text{--}3.8) \times 10^6 \text{ s}^{-1}$; $[\cdot\text{OH}] = 2.72 \times 10^{-6} \text{ M}$.^d $[3,4\text{-Xyleneol}] = 3.0 \times 10^{-4} \text{ M}$; $[\cdot\text{OH}] = 6.01 \times 10^{-6} \text{ M}$.^e $[3,4\text{-Xyleneol}] = 3.0 \times 10^{-4} \text{ M}$; $[\cdot\text{OH}] = 4.34 \times 10^{-6} \text{ M}$.^f $[3,4\text{-Xyleneol}] = 3.0 \times 10^{-4} \text{ M}$; $[\cdot\text{OH}] = 4.26 \times 10^{-6} \text{ M}$.^g $[3,4\text{-Xyleneol}] = (0.5\text{--}2.5) \times 10^{-4} \text{ M}$; $k_{\text{obs}} = (0.83\text{--}1.5) \times 10^6 \text{ s}^{-1}$; $[\cdot\text{OH}] = 1.62 \times 10^{-6} \text{ M}$.^h $[3,4\text{-Xyleneol}] = 3.0 \times 10^{-4} \text{ M}$; $[\cdot\text{OH}] = 4.29 \times 10^{-6} \text{ M}$.ⁱ Observed rate constant for the reaction of 3,4-xyleneol + $\cdot\text{OH}$ as determined from a concentration dependence study at 300 and 415 nm.^j Rate constant for $\cdot\text{OH}$ addition.^k Rate constant for direct electron transfer.^l $[3,4\text{-Xyleneol}] = (0.5\text{--}2.5) \times 10^{-4} \text{ M}$; $k_{\text{obs}} = (8.4\text{--}16) \times 10^5 \text{ s}^{-1}$; $[\cdot\text{OH}] = 1.68 \times 10^{-6} \text{ M}$.^m $[3,4\text{-Xyleneol}] = 3.0 \times 10^{-4} \text{ M}$; $[\cdot\text{OH}] = 4.21 \times 10^{-6} \text{ M}$.ⁿ $[3,4\text{-Xyleneol}] = (0.5\text{--}3.0) \times 10^{-4} \text{ M}$; $k_{\text{obs}} = (7.7\text{--}22) \times 10^5 \text{ s}^{-1}$; $[\cdot\text{OH}] = 1.42 \times 10^{-6} \text{ M}$.^o $[3,4\text{-Xyleneol}] = 3.0 \times 10^{-4} \text{ M}$; $[\cdot\text{OH}] = 4.35 \times 10^{-6} \text{ M}$.^p General conditions: all solutions were buffered with 10^{-3} M phosphate buffer and were N_2O saturated.

data obtained are summarized in Table 5. They are divided into two principal groups: in the range $4 < \text{pH} < 8$ the rate of formation of the phenoxy radical was independent of the initial concentration of 3,4-xyleneol; at $\text{pH} \geq 9$ the observed rate showed a concentration dependence (Fig. 7). In addition, the formation of the phenoxy radical from the $\cdot\text{OH}$ adduct could be monitored spectrophotometrically (Fig. 6 for pH 4) for the first group but not at pH 9 and 10 (Figs. 8 and 9). The 2 ms spectrum of the reaction products (3,4-xyleneol + $\cdot\text{OH}$)

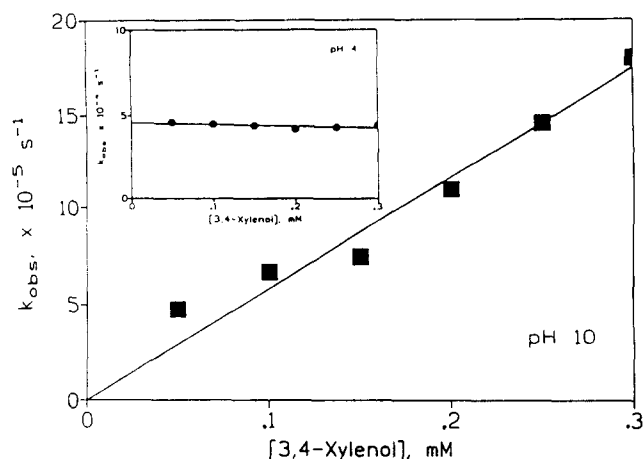


Fig. 7. Dependence of the observed rate constants (415 nm) on the concentration of 3,4-xyleneol in the formation of the 3,4-dimethylphenoxy radical at pH 4 (inset) and 10 at constant $[\cdot\text{OH}]$. The solutions were N_2O saturated; $[\cdot\text{OH}] = 2.72 \times 10^{-6} \text{ M}$ at pH 4; $[\cdot\text{OH}] = 1.42 \times 10^{-6} \text{ M}$ at pH 10.

is similar to the one at pH 4 shown earlier (Fig. 4), except that the relative quantity of the phenoxy radical (absorption band at about 410 nm) is greater. In contrast, with the observations at pH 4 (Fig. 6), even at time scales as short as 20 μs (Fig. 9), there are no indications that the phenoxy radical originates from the $\cdot\text{OH}$ adduct, as the spectra showed no isosbestic point. Interestingly, the cut-off appears somewhere between pH 8 and 9, i.e. at less than 2 pH units from the pK_a of 3,4-xyleneol ($\text{pK}_a = 10.4$) [20].

The pK_a of the dihydroxy-3,4-dimethylcyclohexadienyl radical is around 8, by inference from the work of Draper et al. [19], who noted that the pK_a (4.8) of the dihydroxy-2,4,5-trichlorocyclohexadienyl radical was approximately 2 pK_a units lower than the pK_a (7.4) of the parent 2,4,5-trichlorophenol. Deprotonation of the $\cdot\text{OH}$ adduct should therefore occur readily at $\text{pH} > 8$. The radical anion spectra may have masked the isosbestic point, if any. We infer therefore that at $\text{pH} \leq 8$ the reaction of 3,4-xyleneol with $\cdot\text{OH}$ proceeds by the mechanism described by the upper route of Eq. (11).

At $\text{pH} > 8$ the reaction may conceivably take place by either of two pathways: (i) the mechanism of Eq. (11) with dehydration taking place at a much faster rate than at $\text{pH} \leq 8$; (ii) the reaction proceeding via *inner-sphere* electron transfer from the 3,4-dimethylphenoxide anion to the $\cdot\text{OH}$ radical, Eq. (12). The latter option is consistent with the observation that the rate of formation of the phenoxy radical depended on the initial concentration of 3,4-xyleneol. Values of the observed

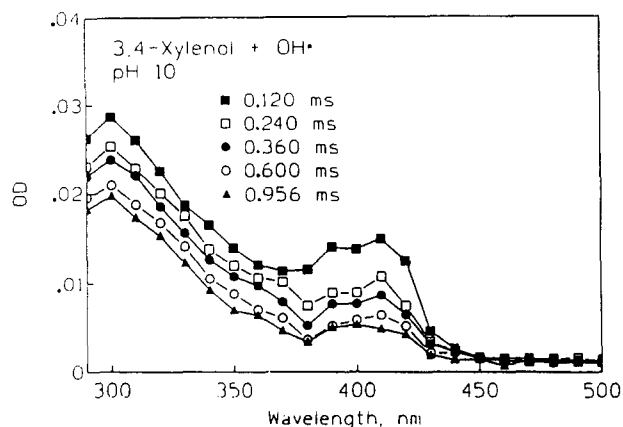


Fig. 8. Transient absorption spectra of the reaction product(s) between 3,4-xylolenol and ·OH monitored at 0.120, 0.240, 0.360, 0.600 and 0.956 ms following irradiation of a 3×10^{-4} M aqueous 3,4-xylolenol solution buffered at pH 10. The solution was N_2O saturated; $[·OH] = 6.10 \times 10^{-6}$ M.

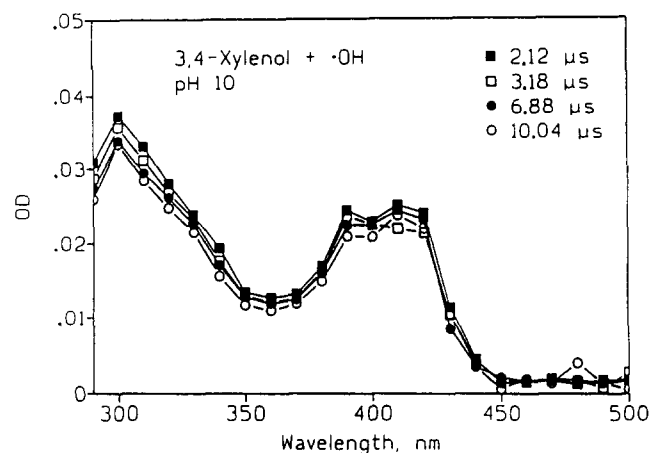
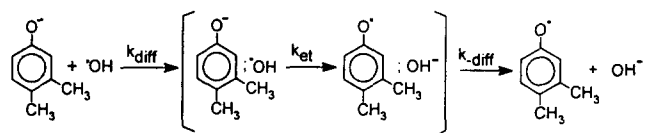


Fig. 9. Transient absorption spectra of the reaction product(s) between 3,4-xylolenol and ·OH monitored at 2.12, 3.18, 6.88 and 10.04 μs following irradiation of a 3.0×10^{-4} M aqueous 3,4-xylolenol solution buffered at pH 10. The solution was N_2O saturated; $[·OH] = 5.97 \times 10^{-6}$ M.

electron transfer rates k_{ET} at pH 9 and 10 are reported in Table 5.



(12)

The formation of phenoxyl radicals by direct *outer-sphere* electron transfer from the phenoxide anion to the ·OH radical is precluded because of unfavourable reorganization energies associated with the ·OH/OH⁻ transformation [30]. However, it is not certain whether the same rationale applies to a surface-bound ·OH/OH⁻ transformation on the surface of a semiconductor (TiO₂) particle. Homogeneous electron transfer via an inner-sphere transition state similar to or different from the ·OH adduct cannot be precluded.

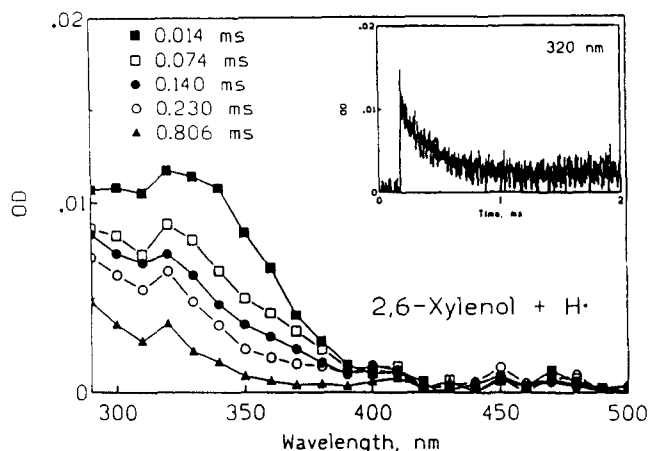
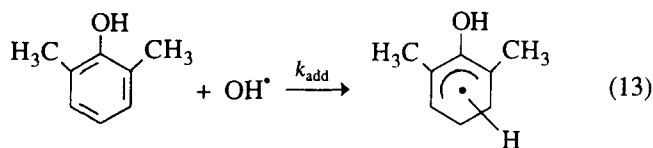


Fig. 10. Transient absorption spectra of the hydroxy-2,6-dimethylcyclohexadienyl radical at 0.014, 0.074, 0.140, 0.230 and 0.806 ms following irradiation of 4.0×10^{-4} M 2,6-xylolenol at pH 1 (buffered) in a 0.2 M *tert*-butyl alcohol aqueous solution. The solution was N_2 saturated; $[H·] = 2.49 \times 10^{-6}$ M. The inset shows the decay of the optical density at 320 nm.

3.3. Reaction with H[·] radicals

3.3.1. Hydroxy-2,6-dimethylcyclohexadienyl radical

The time-resolved absorption spectra of the H atom adduct of 2,6-xylolenol, Fig. 10, are characterized by one absorption band centred at about 320 nm ($\epsilon_{320} = 2500 \pm 300 \text{ M}^{-1} \text{ cm}^{-1}$). The disappearance of the H[·] adduct (320 nm) followed second-order kinetics: $k/[\text{H}·] = (5.6 \pm 1.0) \times 10^5 \text{ s}^{-1}$ and $k_d = (3.5 \pm 0.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The rate of addition of H[·] to 2,6-xylolenol (Eq. (13)) was monitored via the increase in optical density at 320 nm at constant [H[·]] (2.19×10^{-6} M) with various concentrations of 2,6-xylolenol (1.0 – 4.0×10^{-4} M); $k_{obs} = (4.0$ – $7.4) \times 10^5 \text{ s}^{-1}$, from which $k_{add} = (1.1 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The kinetics of formation and decay of the hydroxy-2,6-dimethylcyclohexadienyl radical and its spectral properties confirm its identity and are in good agreement with earlier work on similar substrates [14,29].



(13)

4. Conclusions

Both 2,6- and 3,4-xylolenol react with $N_3^·$ radicals to form the corresponding dimethylphenoxyl radicals; hydrogen atoms react with 2,6-xylolenol to form hydroxy-2,6-dimethylcyclohexadienyl radicals (hydrogen atom adducts).

Reactions of ·OH radicals with five of the six xylolenol isomers produced exclusively the ·OH adducts (dihydroxydimethylcyclohexadienyl radicals) as initial products; subsequent H₂O elimination to yield phenoxyl- or benzylic-type

radicals is not ruled out by the present data. The behaviour of 3,4-xyleneol was somewhat unique; it reacts with $\cdot\text{OH}$ to form both an $\cdot\text{OH}$ adduct and a phenoxyl radical. At $\text{pH} \leq 8$ the 3,4-phenoxyl radical is formed by dehydration of the $\cdot\text{OH}$ adduct; at $\text{pH} \geq 8-9$ both radicals are formed concurrently. The mechanism of the reaction of 3,4-xyleneol with $\cdot\text{OH}$ parallels more the behaviour of phenol and cresol [14] than that of a methylated benzene [29]. Thus the positions of the methyl substituents in the xyleneols bear directly on the reaction mechanism and on the nature of the products.

The results presented here add to our understanding of the events in heterogeneous photocatalysis with irradiated TiO_2 aqueous dispersions, for example. The primary photo-oxidations likely proceed via pathways analogous to those presented here (e.g. Eq. (11)), implicating the $\cdot\text{OH}$ radical, even though analysis of intermediate products would suggest $\cdot\text{OH}$ additions to aromatic rings in all cases [4–9]. Work has begun [10] to address the details of these pathways. A distinction between direct oxidation by *trapped* valence band holes and oxidation via surface-bound $\cdot\text{OH}$ radicals may be a moot point, as the two pathways may not be distinguished experimentally in aqueous media [31].

Acknowledgements

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