PERKIN 2

Reactions of phenol-OH-adduct radicals. Phenoxyl radical formation by water elimination *vs.* oxidation by dioxygen

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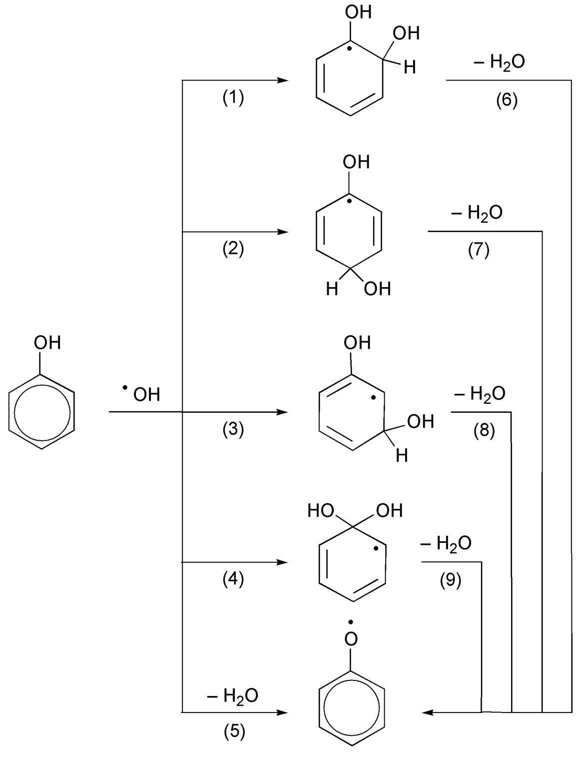
The reactions of OH radicals generated radiolytically in N_2O-saturated aqueous solutions with phenol have been examined, focusing special attention on the addition of dioxygen and the competing dehydration reactions of the OH-adduct radicals. Using the pulse radiolysis technique, the overall rate constant of dioxygen addition to the dihydroxycyclohexadienyl radicals was determined to be $k = 1.2 \times 10^9$ dm^3 mol^{-1} s^{-1}. This dioxygen addition reaction was found to be practically irreversible, in contrast to other hydroxycyclohexadienyl radicals. The so-formed dihydroxycyclohexadienylperoxyl radicals subsequently eliminate $HO_2^{\bullet}/O_2^{\bullet -}$. By using tetranitromethane (TNM) as a probe for $O_2^{\bullet -}$ (formation of the nitroform anion), the overall rate constant of $HO_2^{\bullet}$-elimination (mainly of the *para*- and *ortho*-isomers, formation of hydroquinone and catechol, respectively) was determined to be 1.3×10^5 s^{-1}. The rate constant of the dehydration of the *p*-OH-adduct in neutral to acidic solution was determined by monitoring the absorbance build-up of the phenoxyl radical to be $k_7 = 1.8 \times 10^3 + 1.7 \times 10^9 \times [H^+]$ s^{-1}, and that of the *o*-OH-adduct to be $k_6 = 1.1 \times 10^8 \times [H^+]$ s^{-1} (the uncatalysed reaction is too slow to be measurable by this technique). The HPO_4^{2-}-catalysed dehydration rate constant of the *p*-OH-adduct was similarly determined to be 5.8×10^7 dm^3 mol^{-1} s^{-1}. Based on the above rate constant of dioxygen addition, the rate constant of the proton-catalysed dehydration of the *p*-OH-adduct was determined by the competition of these two reactions on the yield of hydroquinone to be 1.0×10^9 dm^3 mol^{-1} s^{-1}, and similarly that of the *ortho*-OH-adduct (on the yield of catechol) to be 2.1×10^8 dm^3 mol^{-1} s^{-1}.

Although the formation of phenoxyl radicals is thermodynamically favoured,[1] the reaction of OH radicals with phenol mainly leads to the formation of the four isomeric dihydroxycyclohexadienyl radicals (OH-adducts). Being an electrophilic radical,[2] the OH radical preferentially adds to the *ortho*-[reaction (1), 48%] and *para*-positions [reaction (2), 36%].[3] Addition to the *meta*-position [reaction (3)] amounts to only 8%.[3] Addition to the *ipso*-position [reaction (4)] is expected to be quite negligible, and the resulting *ipso*-OH-adduct possibly dehydrates promptly to give the phenoxyl radical [reaction (9)]. The fraction of *ipso*-OH-adduct is therefore not distinguishable from direct H-abstraction by $^{\bullet}OH$ [reaction (5)]. Based on the material balance of OH radicals, their total yield [reactions (4) and (5)] is attributed to the remaining 8% of OH radicals.[3]



The OH-adduct-radicals undergo spontaneous and H^+- and OH^--catalysed elimination of water to yield the more resonance-stabilised phenoxyl radical [reactions (6)–(9)].[4,5] The rate of this dehydration reaction differs among the different isomeric OH-adduct radicals. By monitoring the kinetics of absorbance build-up of the phenoxyl radical at 400 nm, or the decay of the dihydroxycyclohexadienyl radicals at 330 nm under various pH conditions, it has been found that the H^+-catalysed dehydration reaction consists of two parallel processes, a fast and a slow component with approximately equal contributions.[4] More recently, based on the pH dependence of the yields of hydroquinone and catechol in the presence of an oxidant, it has been possible to assign the faster process to the water elimination reaction of the *p*-OH-adduct radical and the slower process to that of the *o*-OH-adduct radical.[3]

Ozonation of drinking- and waste-water is gaining in importance, and in arid countries this technique is now also used in the so-called reclamation process, where municipal waste-water is reprocessed to drinking water. Phenol is very reactive towards ozone [$k(\text{phenol} + O_3) = 1.3 \times 10^3$ dm^3 mol^{-1} s^{-1}; $k(\text{phenolate} + O_3) = 1.4 \times 10^9$ dm^3 mol^{-1} s^{-1}][6,7] and thus is readily degraded.[8–19] We have recently ascertained that the

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major products, catechol and hydroquinone, have, to a large extent, ${}^{\bullet}OH$ as precursor.[20] There are also non-radical processes that lead to singlet dioxygen $[O_2(^1\Delta_g)]$ formation.[21] Free radicals that are formed during ozonation may be oxidised by dioxygen (ozonated solutions are typically rich in dioxygen, because ozone is normally generated from dioxygen; for a review on peroxyl radicals in aqueous solution see ref. 22) or by ozone (*cf.* ref. 23).

For a mechanistic description of the rather complex phenol/O_3/O_2 system, one requires reliable data on the kinetics of the reaction of dioxygen with the phenol–OH-adduct radicals and the competing water-elimination processes. In this context it is of interest to learn whether dioxygen addition to these dihydroxycyclohexadienyl radicals is reversible, as has been found for other hydroxycyclohexadienyl radicals.[24–26] The data to be reported in the present paper have been obtained with the help of radiation techniques, notably pulse radiolysis.

Experimental

Aqueous solutions of phenol (Merck, purified by zone-melting, concentration typically 1×10^{-3} mol dm^{-3}) were prepared in Milli-Q-filtered (Millipore) water and saturated with N_2O or N_2O–O_2 (4 : 1 v/v). γ-Radiolyses were carried out in a panoramic ^{60}Co-source at a dose rate of 0.1 Gy s^{-1} to total doses of up to 270 Gy (*i.e.* the conversion of the substrate remained below 20%). Samples of the irradiated solution were analysed by HPLC on a 25 cm Nucleosil 5-C_{18} column with a 5 cm precolumn. The eluent was an aqueous solution of 25% methanol flowing at 1 cm^3 min^{-1}. The retention times were: hydroquinone, 5 min, catechol, 7.8 min, and phenol, 14.5 min.

Pulse radiolysis was carried out with a 2.8 MeV van-de-Graaff accelerator delivering electron pulses of 0.4 μs duration. Intermediates were monitored by optical detection. The pulse radiolysis set-up has been described previously.[27] For dosimetry, N_2O-saturated 10^{-2} mol dm^{-3} thiocyanate solution was used for optical detection, taking $G \times \varepsilon[(SCN)_2^{\bullet -}] = 4.8 \times 10^{-4}$ m^2 J^{-1} at 480 nm.[28] (Although more recently a 10% higher value for $G \times \varepsilon$ has been redetermined,[29] for consistency with our previous measurements the lower value was used.)

Results and discussion

The radical-generating system

Hydroxyl radicals are generated in the radiolysis of water [reaction (10)]. The radiation-chemical yields (G values) of the

$$H_2O \xrightarrow[\text{radiation}]{\text{ionizing}} e_{aq}^-, {}^{\bullet}OH, H^{\bullet}, H^+, OH^-, H_2O_2, H_2 \quad (10)$$

primary radicals are $G({}^{\bullet}OH) \approx G(e_{aq}^-) = 2.9 \times 10^{-7}$ mol J^{-1}, $G(H^{\bullet}) = 0.6 \times 10^{-7}$ mol J^{-1}, and $G(H_2O_2) \approx 0.7 \times 10^{-7}$ mol J^{-1}. N_2O is used to convert the solvated electron into ${}^{\bullet}OH$ [reaction (11)]. The rate constant of the reaction of hydroxyl radicals

$$e_{aq}^- + N_2O + H_2O \longrightarrow {}^{\bullet}OH + OH^- + N_2 \quad (11)$$

with phenol (pK_a = 10) [reactions (1)–(5)] has been reported to be ~10^{10} dm^3 mol^{-1} s^{-1}.[30]

Conversion of the dihydroxycyclohexadienyl radicals into phenoxyl radicals

The transient spectra observed in the pulse radiolysis of a N_2O-saturated solution of phenol at pH 6.8 (Fig. 1) are in good agreement with the reported observations.[4] Immediately after a 0.4 μs pulse the only prominent absorption comes from the phenol OH-adduct radicals at 330 nm, and very little absorption of the phenoxyl radical at 400 nm[31] is observed.

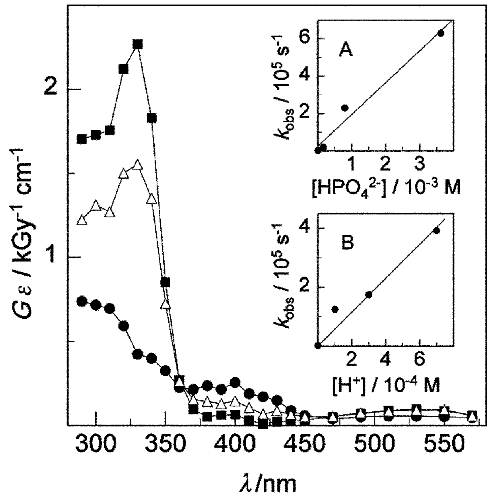


Fig. 1 Pulse radiolysis of a N_2O-saturated solution of phenol (10^{-3} mol dm^3) at pH 6.8. Transient absorption spectra observed 2 μs (■), 30 μs (△) and 200 μs (●) after the pulse (~4 Gy per pulse). Inset A: k_{obs} of absorbance build-up at 400 nm as function of HPO_4^{2-} concentration. Inset B: k_{obs} as function of proton concentration.

Monitored 200 μs after the pulse, the absorption at 400 nm increases at the expense of that at 330 nm. The rate of absorption build-up at 400 nm, as well as the decay at 330 nm, are dose-rate dependent for doses between 1.5 and 10 Gy per pulse, since the bimolecular decay of the radicals is also reflected in the kinetics. By extrapolating the reciprocal of the first half-lives of absorption decay at 330 nm to zero dose, the rate constant of phenoxyl radical formation at neutral pH, $k = 1.8 \times 10^3$ s^{-1} was obtained. A similar value was obtained for the build-up at 400 nm. A higher value (~5×10^3 s^{-1}) has been reported for the uncatalysed dehydration of the dihydroxycyclohexadienyl radicals[4] (a somewhat higher value would be obtained if the experimental data were not corrected for the bimolecular decay of radicals by extrapolation to zero dose). As will be shown below, the dehydration of the *p*-OH-adduct in acidic solution is faster than that of the *o*-OH-adduct. The above rate constant can thus be attributed to the uncatalysed dehydration of the *p*-OH-adduct. The corresponding value for the *o*-OH-adduct would be still lower, and therefore not measurable under pulse radiolysis conditions. By monitoring the absorption decay at 370 nm at varying dose per pulse, the rate constant of bimolecular decay of the OH-adduct radicals was found to be $2k = 2.0 \times 10^8$ dm^3 mol^{-1} s^{-1}. For a compilation of rate constants see Table 1.

At pH < 5, the formation of the phenoxyl radical was observed to consist of two parallel processes, a fast build-up followed by a slower build-up, with approximately equal yields. The rates of these two processes increase with increasing proton concentrations. From the linear plot of the observed first-order rate constant of the first absorption build-up at 400 nm *versus* proton concentration at pH 3.4 to 4.8 (inset B in Fig. 1), the rate constant of the fast H^+-catalysed phenoxyl radical formation was obtained, $k(H^+)_{fast} = 1.7 \times 10^9$ dm^3 mol^{-1} s^{-1}. Similarly, $k(H^+)_{slow} = 1.1 \times 10^8$ dm^3 mol^{-1} s^{-1} was obtained from the second and slower absorption build-up (data not shown), these values are in good agreement with the reported values.[3,4]

The OH^--catalysed dehydration reaction of the OH-adduct radicals of phenol has been reported to be faster than the H^+-catalysed reaction ($k_{obs} > 1 \times 10^5$ s^{-1} at pH 8.6 and 1.05×10^7 s^{-1} at pH ≈ 11).[4,5] Efficient catalysis of water elimination by phosphate buffer has also been observed.[4] By monitoring the absorption build-up at 400 nm with increasing $H_2PO_4^-$ concentration at pH 5.8 to 4.8, we found no catalytic effect of $H_2PO_4^-$. The catalytic effect of phosphate buffer is due solely to the presence of HPO_4^{2-}. The value for the rate constant of the HPO_4^{2-}-catalysed dehydration reaction has been determined

Table 1 Compilation of rate constants determined in the present study

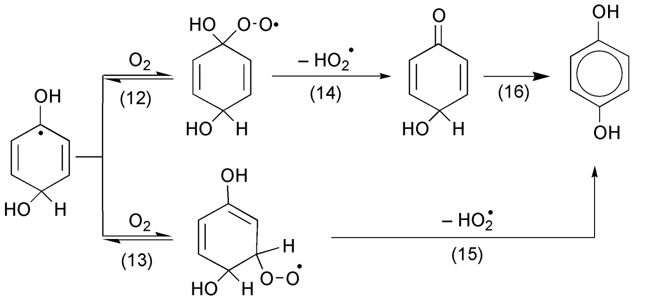
Reaction	Rate constant
2 OH-Adduct radicals$\rightarrow$products	2.0×10^8 dm^3 mol^{-1} s^{-1} (2*k*)
p-OH-Adduct radicals$\rightarrow$phenoxyl + H_2O	1.8×10^3 s^{-1}
p-OH-Adduct radicals$\rightarrow$phenoxyl + H_2O (HPO_4^{2-}-catal.)	5.8×10^7 dm^3 mol^{-1} s^{-1}
p-OH-Adduct radicals$\rightarrow$phenoxyl + H_2O (H^+-catal.)	1.7×10^9 dm^3 mol^{-1} s^{-1} [a]
	1.0×10^9 dm^3 mol^{-1} s^{-1} [b]
o-OH-Adduct radicals$\rightarrow$phenoxyl + H_2O (H^+-catal.)	1.1×10^8 dm^3 mol^{-1} s^{-1} [a]
	2.1×10^8 dm^3 mol^{-1} s^{-1} [b]
OH-Adduct radicals + $O_2$$\rightarrow$peroxyl radicals	1.2×10^9 dm^3 mol^{-1} s^{-1}
Peroxyl radicals$\rightarrow$$HO_2^\bullet$ + products	1.3×10^5 s^{-1}

[a] Determined by pulse radiolysis. [b] Determined by competition kinetics.

in a weakly basic solution of phenol (pH 8.1–8.7) with varying HPO_4^{2-} concentration [the contribution from OH^- has been corrected taking $k(OH^-)^5 = 1 \times 10^{10}$ dm^3 mol^{-1} s^{-1}] to be $k(HPO_4^{2-}) = 5.8 \times 10^7$ dm^3 mol^{-1} s^{-1} (inset A in Fig. 1).

Reaction of the dihydroxycyclohexadienyl radicals with dioxygen

In the presence of dioxygen, the *C*-centered dihydroxycyclohexadienyl radicals will rapidly add dioxygen to yield the corresponding peroxyl radicals [*e.g.*, reactions (12) and (13) for the *p*-OH-radical adduct]. The phenoxyl radical is not known to react with dioxygen (*cf.* ref. 32).



In the pulse radiolysis of a N_2O–O_2 (4 : 1)-saturated solution of phenol at pH 6.8, the initial absorption of the OH-adduct radicals at 330 nm decays rapidly, as these radicals are being converted to the corresponding peroxyl radicals with weaker absorbance at this wavelength. Fig. 2 shows the observed first-order rate constant of absorbance decay at varying dioxygen concentrations.

From the slope the rate constant of dioxygen addition to the dihydroxycyclohexadienyl radicals of $k = 1.2 \times 10^9$ dm^3 mol^{-1} s^{-1} is obtained. There is a small intercept (3.8×10^4 s^{-1}), which includes the contribution (1.8×10^3 s^{-1}) from the dehydration reactions (see above) and the contribution from the bimolecular decay (~10^3 s^{-1} at 6 Gy per pulse), as well as that from the subsequent rapid $HO_2^\bullet$-elimination of the dihydroxycyclohexadienylperoxyl radicals [*cf.*, reactions (14) or (15), see below]. These leave little room for the reverse dioxygen addition reactions [*cf.* reactions (−12) or (−13)]. This is in contrast to the other hydroxycyclohexadienylperoxyl radicals, where the reversibility of the dioxygen addition reaction is much more pronounced.[24–26]

$HO_2^\bullet$-elimination reaction of the the dihydroxycyclohexadienylperoxyl radicals

In the pulse radiolysis of a N_2O–O_2 (4 : 1)-saturated solution of phenol containing tetranitromethane (TNM, 3×10^{-4} mol dm^{-3}), the absorption of the nitroform anion (NF^-) at 350 nm increases rapidly following an initial jump, which is due to the reaction of $HO_2^\bullet$–$O_2^{\bullet -}$ from primary hydrogens [reactions (10), (16) and (17)] with TNM [reaction (18)].

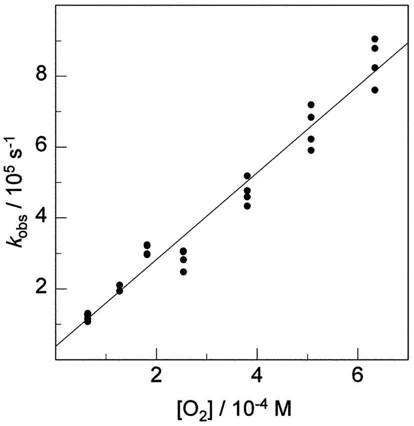


Fig. 2 Dioxygen concentration dependence of the observed first-order rate constant of absorption decay at 330 nm in the pulse radiolysis of a N_2O–O_2 (4 : 1)-saturated solution of phenol at pH 6.8 (~5 Gy per pulse).

$$H^\bullet + O_2 \longrightarrow HO_2^\bullet \qquad (16)$$

$$HO_2^\bullet \rightleftharpoons H^+ + O_2^{\bullet -} \qquad (17)$$

$$O_2^{\bullet -} + C(NO_2)_4 \longrightarrow C(NO_2)_3^- + NO_2 + O_2 \qquad (18)$$

The rate constant of the second step of NF^- formation is 1.3×10^5 s^{-1}. The yield of this absorption build-up corresponds to $G(NF^-) = G(O_2^{\bullet -}) = 4.6 \times 10^{-7}$ mol J^{-1}, or 80% of $^\bullet OH$. The yield of $O_2^{\bullet -}$ corresponds approximately to the sum of the *o*- and *p*-OH-adduct radicals. Since reaction (18) is not the rate-determining step ($k_{18} = 1.9 \times 10^9$ dm^3 mol^{-1} s^{-1}),[33] the rate constant determined above (1.3×10^5 s^{-1}) is thus the overall rate of $HO_2^\bullet$-elimination of the peroxyl radicals of these two isomeric dihydroxycyclohexadienyl radicals [*e.g.*, reactions (14), (15) of the *p*-OH-adduct-radical].

Product studies

$HO_2^\bullet$-elimination reactions of the peroxyl radicals of the *o*- and *p*-OH-adducts yield catechol and hydroquinone, respectively [*cf.* reactions (14)–(16) for the formation of hydroquinone]. In the steady state γ-radiolysis of a N_2O–O_2 (4 : 1)-saturated solution of phenol at pH 6.8, we found $G(\text{catechol}) = 2.3 \times 10^{-7}$ mol J^{-1} and $G(\text{hydroquinone}) = 1.8 \times 10^{-7}$ mol J^{-1}. In acidic solution, the water elimination reactions (6) and (7) become faster with increasing H^+ concentration and compete with dioxygen addition. Based on this competition between the proton-catalysed water elimination and dioxygen addition, one can write eqn. (19) for the formation of hydroquinone, which can be rearranged to give eqn. (20). An analogous equation may be written for the formation of catechol.

$$G(\mathrm{HQ}) = f\,G(p\text{-OH-A}) \times \frac{k_{12,13}[\mathrm{O_2}][p\text{-OH-A}]}{k_{12,13}[\mathrm{O_2}][p\text{-OH-A}] + k_7[\mathrm{H^+}][p\text{-OH-A}]} \quad (19)$$

$$\frac{G(\mathrm{HQ})_\mathrm{o}}{G(\mathrm{HQ})} - 1 = \frac{k_7[\mathrm{H^+}]}{k_{12,13}[\mathrm{O_2}]} \quad (20)$$

Here $G(\mathrm{HQ})_\mathrm{o}$ is the G value of hydroquinone formation in the absence (*i.e.* lowest H^+ concentration at neutral pH) and $G(\mathrm{HQ})$ in the presence of H^+. The term f denotes the fraction of the reactions of the p-OH-adduct radicals (abbreviated as p-OH-A) that leads to the formation of hydroquinone.

A plot of $G(\mathrm{HQ})_\mathrm{o}/G(\mathrm{HQ}) - 1$ *vs.* the proton concentration (Fig. 3) yields a straight line with a slope of 3.1×10^3 dm^3 mol^{-1}. Taking $k_{12,13}(\mathrm{O_2} + p\text{-OH-A}) = 1.2 \times 10^9$ dm^3 mol^{-1} s^{-1} (see above), $k_7 = 1.0 \times 10^9$ dm^3 mol^{-1} s^{-1} is obtained. The analogous plot for the formation of catechol is also shown in Fig. 3, and based on the same assumptions $k_6 = 2.1 \times 10^8$ dm^3 mol^{-1} s^{-1} is obtained. The value of k_7 obtained in this way is somewhat lower than the value [$k(\mathrm{H^+})_\mathrm{fast} = 1.7 \times 10^9$ dm^3 mol^{-1} s^{-1}] obtained above by pulse radiolysis, but is in good agreement with the reported value for k(dehydration) ($\sim 1 \times 10^9$ dm^3 mol^{-1} s^{-1}) of the p-dihydroxycyclohexadienyl radicals.[3] On the other hand, the value of k_6 obtained here is higher than the value of $k(\mathrm{H^+})_\mathrm{slow}$ obtained above by pulse radiolysis and the reported value (both $\sim 1 \times 10^8$ dm^3 mol^{-1} s^{-1})[3] for the dehydration of the o-dihydroxycyclohexadienyl radicals.

It is noted that the yields using dioxygen as an oxidant are lower (catechol 40% of $^\bullet$OH, hydroquinone 31% of $^\bullet$OH) than when p-benzoquinone was used to oxidize the dihydroxycyclohexadienyl radicals (catechol 48% of $^\bullet$OH, hydroquinone 36% of $^\bullet$OH).[3] This relative difference of 13% is significant (*i.e.* not within experimental error), and we conclude that in the case of dioxygen other reactions besides $HO_2^\bullet$-elimination reactions may proceed, albeit to a much lower extent than observed with other aromatic compounds, *e.g.*, benzene[25] or terephthalate.[34] In the benzene study,[25] material balance has been obtained, and from the products that are formed under these conditions it has been concluded that peroxyl radicals of the kind formed in reactions (12) or (13) can also undergo intramolecular endoperoxide formation and subsequent fragmentation. In the present system, the $HO_2^\bullet$-elimination is so fast that this process will contribute less to the overall decay processes.

Relevance for the reaction of ozone with phenol

In the ozonation of phenol in aqueous solutions, catechol and hydroquinone are major products.[20] At neutral pH, their formation is suppressed when *tert*-butyl alcohol (which has a very low reactivity towards ozone)[7] is added to scavenge $^\bullet$OH. Upon lowering the pH, the hydroquinone and catechol yields decrease (hydroquinone more affected), as in the case of $^\bullet$OH (see above). At pH 2, their formation ceases completely. This strongly points to the importance of $^\bullet$OH in the ozonation of phenol. Similarly, but to a lesser extent, $^\bullet$OH formation has also been observed in the reaction of ozone with some tertiary amines.[35] When $^\bullet$OH reacts with *tert*-butyl alcohol, formaldehyde is formed in yields close to 30% with respect to $^\bullet$OH.[36,37] In the ozonation of phenol in the presence of *tert*-butyl alcohol, we found that the formaldehyde yield (~10% with respect to ozone reacted with phenol/phenolate) did not change noticeably with pH. This is a strong indication that $^\bullet$OH formation is due to the reaction of ozone with phenol and, as such, does not require the presence of phenolate in equilibrium in the solution [pK_a(phenol) = 10; note that the rate constants of phenolate and phenol differ by six orders of magnitude, *i.e.* phenolate reactions may dominate down to fairly low pH values]. However, one open question remains, that is whether $O_3^{\bullet -}$ (precursor of $^\bullet$OH) is formed directly by electron transfer from phenol to ozone, or whether a phenol–ozone adduct is formed, which releases $O_2^{\bullet -}/HO_2^\bullet$ to react with ozone yielding $O_3^{\bullet -}$ [$k(O_2^{\bullet -} + O_3) = 1.6 \times 10^9$ dm^3 mol^{-1} s^{-1}].[7]

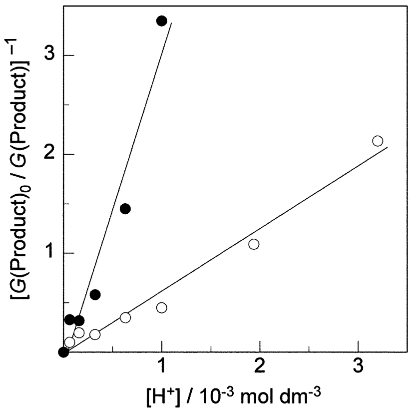


Fig. 3 Proton concentration dependence of the term $G(\mathrm{Product})_\mathrm{o}/G(\mathrm{Product}) - 1$ in the γ-radiolysis of a N_2O–O_2 (4 : 1)-saturated solution of phenol, (●) Product = hydroquinone, (○), Product = catechol.

Considering the fast elimination of $O_2^{\bullet -}/HO_2^\bullet$ from the peroxyl radicals formed upon dioxygen addition to the OH-adduct radicals of phenol, a chain reaction can be induced. This makes it difficult to assess without further experiments the primary yield of the OH-radical-forming process. According to our scavenging experiments with *tert*-butyl alcohol the overall contribution of $^\bullet$OH to phenol degradation is ~30%.

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