Impact of substitution on reactions and stability of one-electron oxidised phenyl sulfones in aqueous solution

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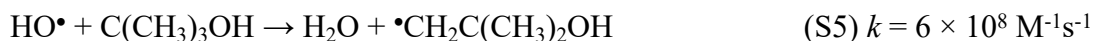
Supporting Information

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1. Competing reactions in the pulse radiolysis experiments

Hydrated electrons react with $S_2O_8^{2-}$ to form tetraoxidosulfate radical anions ($SO_4^{\bullet-}$), reaction (S1).[1] At lower pH there is competition by reaction (S2).[2] The formed $H^\bullet$ may theoretically also react with $S_2O_8^{2-}$, reaction (S3). However the reaction is rather slow.[1,3]

$S_2O_8^{2-} + e_{aq}^- \rightarrow SO_4^{\bullet-} + SO_4^{2-}$	(S1) $k = 1.2 \times 10^{10}$ M^{-1}s^{-1}
$e_{aq}^- + H^+ \rightarrow H^\bullet$	(S2) $k = 2 \times 10^{10}$ M^{-1}s^{-1}
$S_2O_8^{2-} + H^\bullet \rightarrow SO_4^{\bullet-} + SO_4^{2-} + H^+$	(S3) $k = 2 \times 10^7$ M^{-1}s^{-1}

In N_2O-saturated aqueous solutions (24.8 mM at 20 °C) $e_{(aq)}^-$ can be converted to $HO^\bullet$, (reaction S4).[1] We use *t*-BuOH as scavenger if reactions with $HO^\bullet$ should be suppressed, reaction (S5).[1]

$N_2O + H_2O + e_{(aq)}^- \rightarrow N_2 + HO^\bullet + HO^-$	(S4) $k = 9.1 \times 10^9$ M^{-1}s^{-1}
$HO^\bullet + C(CH_3)_3OH \rightarrow H_2O + {}^\bullet CH_2C(CH_3)_2OH$	(S5) $k = 6 \times 10^8$ M^{-1}s^{-1}

All our kinetics experiments were carried our anaerobically, because dioxygen reacts very fast with carbon-centred radicals and interferes with the processes to be observed.

Apart from direct addition to aromatic compounds, reaction (5), $HO^\bullet$ can oxidize aliphatic groups, for example reactions (S5) and (S6). Also direct electron transfer from aromatic groups is conceivable (S7). However, these reactions are at least an order of magnitude slower than reaction (5). Reactions (S6) and (S7) may, therefore, lower the yield of reaction (5) by <10%.

$ArCH_2R + HO^\bullet \rightarrow ArCH^\bullet R + H_2O$	(S6)
$Ar + HO^\bullet \rightarrow Ar^{\bullet+} + OH^-$	(S7)
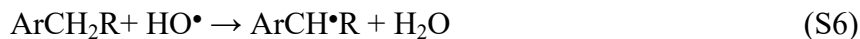
2. Radiochemical yield of intermediates at low pH

If an argon-saturated solution of 10 mM BMPS, 100 mM $K_2S_2O_8$ and 10 mM H_2SO_4 is pulse irradiated, reaction (S2) may compete effectively with reaction (S1). The yield of $H^\bullet$ is increased ($G_{H^\bullet} = 0.116$ µmol J^{-1} instead of 0.06 µmol J^{-1} at pH=7), $G_{Ar(-H)^\bullet} = 0.116$ µmol J^{-1}. With the concominantly decreased yield of $SO_4^{\bullet-}$ ($G_{SO4^{\bullet-}} = 0.224$ µmol J^{-1} instead of 0.28 µmol J^{-1}), the radiochemical yield of reaction (5) is decreased, too: $G_{Ar^{\bullet+},direct} = 0.224$ µmol J^{-1}. The radiochemical yield $HO^\bullet$ is unaffected ($G_{HO^\bullet} = 0.28$ µmol J^{-1}), therefore $G_{Ar(-HO)^\bullet} = 0.28$ µmol J^{-1} and cation radicals can be formed indirectly via equilibrium (6) with $G_{Ar^{\bullet+},indirect} \leq 0.28$ µmol J^{-1}.

The overall yield of cation radicals is therefore $G_{Ar^{\bullet+},total} = G_{Ar^{\bullet+},direct} + G_{Ar^{\bullet+},indirect} \leq 0.504$ µmol J^{-1}.

Under the, probably incorrect, assumption of equilibrium (6) being fully on the side of cation radicals and no other species absorbing at 450 nm, we calculate $\varepsilon_{450nm}(Ar^{\bullet+}) \approx 3 \times 10^3$ $M^{-1}cm^{-1}$.

In the presence of 900 mM t-BuOH reaction (4) is quantitatively suppressed, $G_{Ar(-HO)^\bullet} = 0$ µmol J^{-1}, with a calculated radiochemical yield $G_{Ar^{\bullet+},total} = G_{Ar^{\bullet+},direct} = 0.224$ µmol J^{-1}. This is 60% lower than in absence of t-BuOH and is experimentally observed, see Fig. 2 and Fig. S1.

3. Radiochemical yield in presence of Ce(III)

Ce(III) reacts with $HO^\bullet$, reaction (S8).[4] However, the reaction of $HO^\bullet$ addition with BPS or BMPS is at least one order of magnitude faster.[5] With [BPS] =10 mM or [BMPS] = 10 mM and [Ce(III)] = 0 – 5 mM, reaction (S8) has a yield lower than 5% which negligible for our considerations.

$$Ce(III) + HO^\bullet + H^+ \rightarrow Ce(IV) + H_2O \qquad\qquad (S8)\ k = 3 \times 10^8\ M^{-1}s^{-1}$$

4. Radiochemical yield of ABTS$^{\bullet-}$

In N_2O-saturated solutions of 10 mM BMPS, 0.5 mM ABTS, 300 mM $NaClO_4$ and 10 mM H_2SO_4 reaction (S2) competes with reaction (S4) and reduces the radiochemical yield of $HO^\bullet$ to $G_{HO^\bullet} = 0.399$ µmol J^{-1}. ABTS reacts with $HO^\bullet$ with a rate constant of 1.2×10^{10} $M^{-1}s^{-1}$.[6]

$$ABTS^{2-} + HO^\bullet \rightarrow ABTS^{\bullet-} + H_2O \qquad\qquad (S9)\ k = 1.2 \times 10^{10}\ M^{-1}s^{-1}$$

BPS and HO$^\bullet$ react with a rate constant of 3.2×10^9 M^{-1}s^{-1},[5] and we assume the rate constant for BMPS to have the same value. In the absence of reaction (10) we, therefore, expect $G_{ABTS^{\bullet-}} = 0.067$ µmol J^{-1} and $G_{BMPS^{\bullet+}} = 0.332$ µmol J^{-1}.

With the absorbance as measured in Fig. 4 and $\varepsilon_{650nm}(ABTS^{\bullet-}) = 13000$ M^{-1}cm^{-1} we calculate $G_{ABTS^{\bullet-}} = 0.29$ µmol J^{-1}.[7] The yield of reaction (10) then is $(0.29 - 0.067) / 0.332 = 67\%$. At pH $= 2$ equilibrium (7) will not be fully on the side of cation radicals. Cyclohexadienyl radicals are reducing and may react quickly with ABTS$^{\bullet-}$. We consider the calculated yield of 67% for reaction (10) as lower limit.

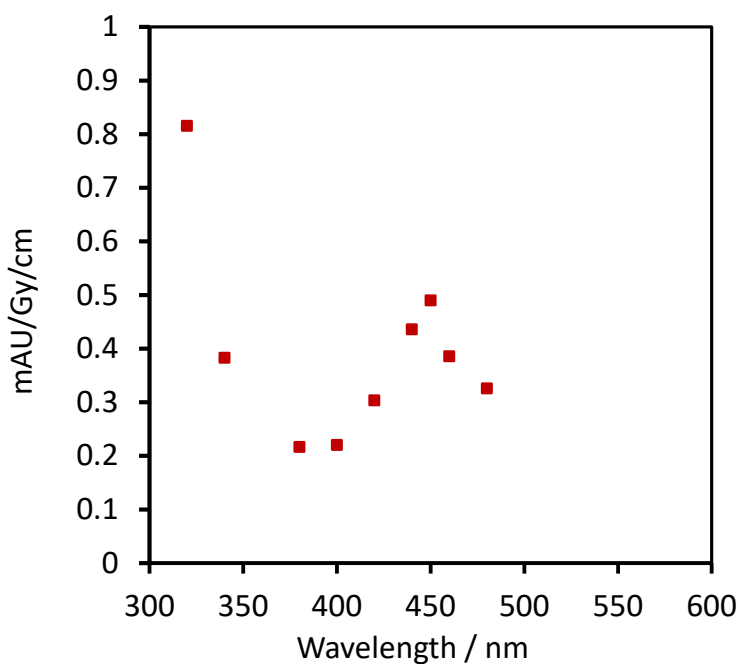## 5. Additional pulse radiolysis and γ-radiolysis experiments

Fig. S1. Transient absorption spectra 5 µs after the pulse (dose 12–32 Gy), obtained from time-resolved absorbance readings, normalized to 1 Gy, measured in argon-saturated solutions that contained 10 mM BMPS, 0.1 M K$_2$S$_2$O$_8$, 900 mM *t*-BuOH and 10mM H$_2$SO$_4$ (red squares).
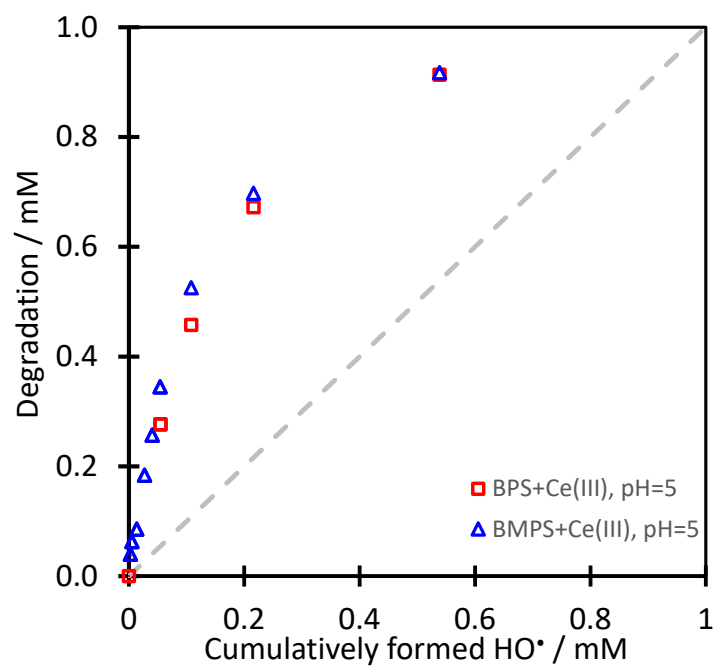
Fig. S2. Degree of degradation of air-saturated solutions of 1 mM BMPS or 1 mM BPS as a function of the total amount of formed HO• at pH=5 in the presence of 0.01 mM Ce(III) and 1 mM H_2O_2 (blue triangles and red squares), ionic strength was adjusted with 0.333 M Na_2SO_4.

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