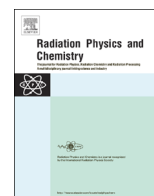




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The influence of radical transfer and scavenger materials in various concentrations on the gamma radiolysis of phenol

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H I G H L I G H T S

- Dissolved O₂ alone (no additives) enhanced the degradation rate of phenol.
- *t*-BuOH, HCOOH and HCOO⁻ reduced the degradation rates in O₂-saturated solutions.
- *t*-BuOH, HCOOH slightly increased the efficiency of degradation in O₂-free solutions.
- HO₂[•] and O₂^{•-} have only a minor contribution to the transformation of PhOH.
- Suggested order of reactivity of organic radicals with phenol: *t*-•BuOH > •COOH > CO₂^{•-}.

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The influence of a radical scavenger (*tert*-butanol (*t*-BuOH)) and two radical transfer materials (formic acid (HCOOH) and formate anion (HCOO⁻)) on the radical set during radiolysis of a simple model compound, phenol (PhOH, 1.0×10^{-4} mol L⁻¹) is discussed in this study. PhOH solutions were irradiated with γ-rays, in the presence of 1.0×10^{-3} , 5.0×10^{-2} and 5.0×10^{-1} mol L⁻¹ *t*-BuOH, HCOOH or HCOONa under deoxygenated and O₂-saturated reaction conditions. The rate of transformation of PhOH increased significantly in the presence of dissolved O₂. The radical transfer or scavenger materials used reduced the rates of transformation of PhOH in O₂-saturated solutions to a similar degree. The simultaneous presence of O₂ and the organic additives in excess proportionally to PhOH results in the conversion of the radical set to less reactive intermediates (*t*-•OOBuOH, HO₂[•] or O₂^{•-}), which made minor contribution to the transformation of PhOH. Under oxygenated conditions, *t*-BuOH and HCOOH in low concentrations slightly promoted the degradation, as opposed to HCOO⁻ which reduced it. However, using higher additive concentrations, their competitive reactions for the primary intermediates came into prominence, thus they reduced the efficiency of PhOH decomposition. HO₂[•] and O₂^{•-}, and also the carbon-centred radicals formed (order of their reactivity *t*-•BuOH > •COOH > CO₂^{•-}) have only a minor contribution to the degradation of PhOH, and the reactions of •OH + PhOH and e_{aq}⁻ + PhOH are the significant processes.

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1. Introduction

Nowadays one of the most important aims of environmental

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sciences is the purification of various wastewaters. Promising alternative methods are the combination of the traditional wastewater treatment technologies with the advanced oxidation processes (AOPs), for example with high energy ionizing radiation treatment. The AOPs are based on reactions initiated by reactive radicals. One of the keys to the development of radiolysis and other AOPs is the understanding of the roles and relative contributions of various reactive species to the transformation of organic substances. In multicomponent systems, the efficiency of the transformation of target substances depends strongly on the

competition for the various reactive species. Additionally, the presence of organic substances can create new pathways for the transformations due to the formation of new reactive species.

Radical-based reactions of the target compounds are strongly affected by the presence of various radical transfer and/or scavenger materials. An interesting question is the effect of dissolved O_2 on the radical set in these multicomponent systems. The aim of this work was to investigate the effects of dissolved O_2 and the influence of *t*-BuOH as radical scavenger, and HCOOH and $HCOO^-$ as radical transfer materials on the degradation of phenol (PhOH) as a simple model substance during its γ radiolysis. Another goal of this study was to investigate the effect of concentration of the radical transfer and/or scavenger materials in excess, these materials were applied in three different concentrations (1.0×10^{-3} , 5.0×10^{-2} and $5.0 \times 10^{-1} \text{ mol L}^{-1}$). PhOH concentration in all cases was $1.0 \times 10^{-4} \text{ mol L}^{-1}$.

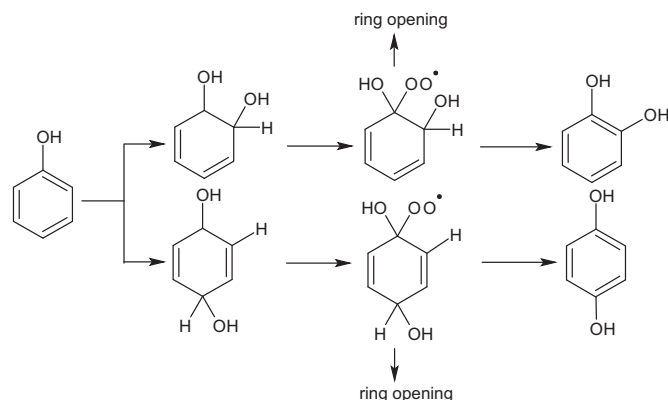
During γ -irradiation of aqueous solutions the decomposition of water molecules results in $\bullet OH$, e_{aq}^- (in lower yield) H^\bullet as reactive primary intermediates (Eq. (1)). In dilute solutions these species may react with solute molecules with *G*-values of 0.280, 0.280 and $0.062 \mu\text{mol J}^{-1}$, respectively (Buxton, 2004; Spinks and Woods, 1990).



In the presence of dissolved O_2 hydroperoxyl radical (HO_2^\bullet) or superoxide radical anion ($O_2^{\bullet -}$) are also present. The reactions of radical transfer and/or scavenger materials with primary radicals and the further transformations of the additives can result in species which can open further, new reaction pathways or shift the ratios of the existing ones towards the transformation of the target compound (Alam et al., 2003; Getoff, 1996). When these additional compounds transform to highly reactive intermediates, they are called radical transfer materials, the additive is referred to as a radical scavenger material when its further transformation results in the formation of low reactivity species that do not contribute to the transformation of the target compound.

In reaction with PhOH $\bullet OH$ adds preferably, due to its electrophilic nature in *ortho* and *para* position (Mvula et al., 2001) (rate constant: $k=8.4 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ (Bonin et al., 2007)) forming dihydroxy cyclohexadienyl radicals. In the absence of dissolved O_2 these radicals may transform to phenoxyl radicals by water elimination. In its presence these reactions are in competition with peroxy radical forming reactions which may result in 1,2- or 1,4-dihydroxyphenols via HO_2^\bullet elimination (Scheme 1) (von Sonntag and Schuchmann, 1997), the peroxy radicals may also undergo ring opening fragmentation reactions.

may add to aromatic ring in a reversible process, albeit the rate constant is rather low ($k=3.0 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ (Lai and Freeman,



Scheme 1. Formation of 1,2- or 1,4-dihydroxyphenols during the reactions of dihydroxy cyclohexadienyl radicals with dissolved O_2 via HO_2^\bullet elimination.

Table 1
Reaction rate constants of primary intermediates with PhOH, and the applied radical transfer or scavenger materials.

	$\bullet OH$	e_{aq}^-	H^\bullet
PhOH	8.4×10^9 ^a	3.0×10^7 ^b	1.7×10^9 ^c
O_2	–	1.9×10^{10} ^c	1.2×10^{10} ^c
<i>t</i> -BuOH	6.0×10^8 ^c	$< 4.0 \times 10^5$ ^d	1.7×10^5 ^e
HCOOH	1.3×10^8 ^c	1.4×10^8 ^f	4.4×10^5 ^c
$HCOO^-$	3.2×10^9 ^c	8.0×10^3 ^g	2.10×10^8 ^c

^a (Bonin et al., 2007).

^b (Lai and Freeman, 1990).

^c (Buxton et al., 1988).

^d (Koehler et al., 1985).

^e (Smaller et al., 1971).

^f (Gordon et al., 1963).

^g (Schwarz, 1992).

1990)), the adduct can be stabilized by protonation, yielding the hydroxyl cyclohexadienyl radical from PhOH. This radical may also form in H^\bullet addition to PhOH ($k=1.7 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ (Buxton et al., 1988)).

Alcohols such as methanol, ethanol, propanol, etc. usually behave as radical transfer and/or scavenger materials (Alam et al., 2001, 2003; Nie et al., 2008; Rong and Sun, 2015; Xiao et al., 2013). *t*-BuOH is one of the $\bullet OH$ scavenger alcohols, its reaction with $\bullet OH$ has a high rate constant, *t*-BuOH is practically unreactive with e_{aq}^- and H^\bullet (Table 1). H-abstraction from *t*-BuOH results in 2,2-dimethyl-2-hydroxyethyl radical (*t*- $\bullet BuOH$), which is assumed to have low reactivity towards organic compounds (Alam et al., 2001). In the presence of dissolved O_2 , *t*- $\bullet BuOH$ transforms to its respective peroxy radical (*t*- $\bullet OOBuOH$) ($k=1.4 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ (von Piechowski et al., 1992)) which may have even lower reactivity (Mark et al., 1990; von Sonntag and Schuchmann, 1997).

HCOOH and $HCOO^-$ form a conjugate acid–base pair ($pK_a=3.75$ (Karpel Vel Leitner and Dore, 1996)) and they also operate as radical transfer materials because of their reactions with $\bullet OH$, e_{aq}^- and H^\bullet (Table 1), the transfer result in carbon-centred radicals (carboxyl radical ($\bullet COOH$) and carboxyl radical anion ($CO_2^{\bullet -}$)) (Flyunt et al., 2001; Getoff and Schenck, 1968; Karpel Vel Leitner and Dore, 1996; von Sonntag and Schuchmann, 1997; Xiao et al., 2013). $\bullet COOH$ and $CO_2^{\bullet -}$ in reaction with O_2 undergo transformation to HO_2^\bullet and $O_2^{\bullet -}$, respectively ($k=3.0 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ (Karpel Vel Leitner and Dore, 1996), $k=4.2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ (Ilan and Rabani, 1976)). Therefore, in the presence of both dissolved O_2 and HCOOH or $HCOO^-$ all of the primary reactive intermediates transform to HO_2^\bullet or $O_2^{\bullet -}$. According to the pK_a of HO_2^\bullet ($pK_a=4.8$ (Bielski et al., 1985)), HO_2^\bullet dominates at low pH in the presence of HCOOH in great excess, at high pH using sodium formate ($HCOONa$) in excess $O_2^{\bullet -}$ is the predominant reactive intermediate.

2. Materials and methods

2.1. Materials

During the experiments 250 mL $1.0 \times 10^{-4} \text{ mol L}^{-1}$ aqueous PhOH (Sigma-Aldrich, $\geq 99\%$) solutions were irradiated. The samples contained 1.0×10^{-3} , 5.0×10^{-2} and $5.0 \times 10^{-1} \text{ mol L}^{-1}$ *t*-BuOH (VWR, 100.0%), HCOOH (AnalR NormaPUR, 99–100%) or $HCOONa$ (FLUKA, 99.0%) prepared in ultrapure MILLI-Q water (ELGA option 4). To investigate the effect of dissolved O_2 , the solutions were purged with either N_2 (Messer, $> 99.99\%$ purity) or O_2 (Messer, $> 99.99\%$ purity, resulting in a dissolved O_2 concentration of $1.25 \times 10^{-3} \text{ mol L}^{-1}$) at a flow rate of 600 mL min^{-1} . The injection of the gas was started 20 min before each experiment, and was continued throughout the irradiation.

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