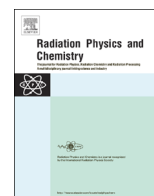




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The influence of radical transfer and scavenger materials in various concentrations on the gamma radiolysis of phenol

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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 $1.0 \times 10^{-4} \text{ mol L}^{-1}$.

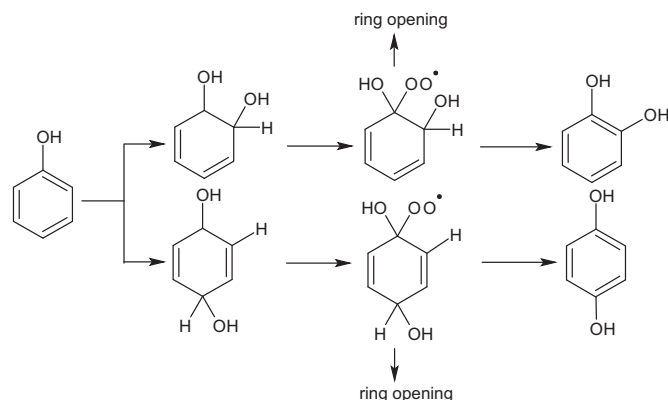
During γ -irradiation of aqueous solutions the decomposition of water molecules results in $\bullet OH$, e_{aq}^- (in lower yield) H^\bullet as reactive primary intermediates (Eq. (1)). In dilute solutions these species may react with solute molecules with *G*-values of 0.280, 0.280 and $0.062 \mu\text{mol J}^{-1}$, 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 ($t\text{-}\bullet BuOH$), which is assumed to have low reactivity towards organic compounds (Alam et al., 2001). In the presence of dissolved O_2 , $t\text{-}\bullet BuOH$ transforms to its respective peroxy radical ($t\text{-}\bullet OOBuOH$) ($k=1.4 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ (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.

2.2. Experimental setup

The 250 mL reservoir was placed in the centre of a SSL-01 panoramic type ^{60}Co - γ source with a dose rate of 11.6 kGy h^{-1} . The solutions in the thermostated reservoir ($25.0 \pm 0.5 \text{ }^\circ\text{C}$) were continuously mixed by N_2 or O_2 bubbling. The irradiations were started by lifting up the ^{60}Co - γ source into the irradiation chamber and at different adsorbed doses ($0.5 - 1.0 - 2.0 - 4.0 - 6.0 - 8.0 \text{ kGy}$) samples were taken from the reservoir. The pH changes during the irradiation were followed with a METTLER TOLEDO MP225 type pH metre.

2.3. Analytical methods-high performance liquid chromatography (HPLC)

The concentration of PhOH was traced by an Agilent 1100 Series high-performance liquid chromatograph with UV detection, using a reverse phase RP-18 column (LiChroCART[®] 150-4.6) with $5 \mu\text{m}$ particle size. The mobile phase contained 35% methanol (VWR, 99.80%) and 65% ultrapure MILLI-Q water (MILLIPORE Milli-Q Direct 8/16) at a flow rate of 0.8 mL min^{-1} at $25 \text{ }^\circ\text{C}$. $20 \mu\text{L}$ samples were analyzed at 210 nm quantification wavelength.

3. Results and discussion

3.1. Influence of dissolved O_2

In the deoxygenated solution the yield of PhOH disappearance is low (Table 2), it is just about 10% of the total primary radical yield, and about 20% of the $\bullet\text{OH}$ yield. The low yield may be due to the reactions of the primarily formed water radiolysis intermediates with each other (e.g., $\bullet\text{OH} + e_{\text{aq}}^- \rightarrow \text{}^-\text{OH}$, $k = 3.1 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ (Christensen et al., 1994)) and not with PhOH. Additionally, one assumes that radical adducts of PhOH have some tendency to transform back to PhOH molecules (Wojnárovits and Takács, 2008). The first points of the dose-dependence curves – due to technical reasons – were taken at relatively high conversions. Once degradation products are also in the solution, they compete for the primary intermediates with the intact PhOH molecules decreasing the extent of PhOH degradation.

As Table 2 shows the G-values of PhOH degradation are significantly higher in oxygenated solution than in the deoxygenated case. In oxygenated solutions the dissolved O_2 reacts with e_{aq}^- and H^\bullet ($e_{\text{aq}}^- + \text{O}_2 \rightarrow \text{O}_2^{\bullet-}$, $k = 1.9 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$; $\text{H}^\bullet + \text{O}_2 \rightarrow \text{HO}_2^\bullet$, $k = 1.2 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ (Buxton et al., 1988)) and results in enhanced $\bullet\text{OH}$ concentration. Since $\text{O}_2^{\bullet-}$ and HO_2^\bullet have low reactivities with PhOH ($k = 5.8 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$ (Tsujiimoto et al., 1993), $k = 2.7 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$ (Kozmér et al., 2014)), the degradation of PhOH is entirely attributed to $\bullet\text{OH}$ reactions. The increase in the degradation rate is partly attributed to the reaction of O_2 and

hydroxyl cyclohexadienyl radical, which reduces the possibility for back reaction to PhOH.

In deoxygenated solutions the original pH remains unchanged upon irradiation around ~ 6.7 , whereas in the oxygenated system the pH gradually decreases with the dose to about 4. This acidification can be explained by the formation of various aliphatic organic acids formed during the ring opening reactions of PhOH.

3.2. Influence of *t*-BuOH

t-BuOH is an often applied $\bullet\text{OH}$ scavenger in scientific investigations, because it reacts with $\bullet\text{OH}$ with a substantially high rate constant (Table 1) forming a non-reductive radical (*t*- $\bullet\text{BuOH}$), as opposed to other alcohols, for instance methanol, ethanol or isopropanol. This additive has negligible reactivity with e_{aq}^- and H^\bullet . The pH of the solutions containing *t*-BuOH changed similarly as in the experiments without this additive, both in the absence and in presence of O_2 .

In solutions with 1.0×10^{-3} , 5.0×10^{-2} and $5.0 \times 10^{-1} \text{ mol L}^{-1}$ *t*-BuOH concentrations, the alcohol competes with PhOH for $\bullet\text{OH}$, and the percentage of $\bullet\text{OH}$ reacting with PhOH is 58, 3 and 0.3%, respectively, calculated by the relation in Eq. (2).

$$\text{Percentage} = 100 \times \frac{k_x[\text{PhOH}]}{k_x[\text{PhOH}] + k_y[\text{radical transfer or scavenger material}]} \quad (2)$$

where k_x and k_y are the reaction rate constants of the reactive water radiolysis intermediate with PhOH and with the radical transfer or scavenger molecules (Table 1).

As Fig. 1a shows, at low doses in O_2 -free solutions *t*-BuOH has not significant effect on the degradation rate of PhOH, however with the increase of the dose the effect becomes higher. In solution containing $1.0 \times 10^{-3} \text{ mol L}^{-1}$ *t*-BuOH, e_{aq}^- reacts mainly with PhOH (42%) and H_3O^+ (52%) ($e_{\text{aq}}^- + \text{H}_3\text{O}^+ \rightarrow \text{H}^\bullet + \text{H}_2\text{O}$, $k = 2.4 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ (Shiraishi et al., 1994)), and H^\bullet formed reacts almost exclusively with PhOH. At 5.0×10^{-2} and $5.0 \times 10^{-1} \text{ mol L}^{-1}$ *t*-BuOH concentration the majority of $\bullet\text{OH}$ reacts with the additive. However, the rate of degradation of PhOH remained also significant in these two cases (Table 2), which shows that the loss of reactive primary intermediates reacting with the *t*-BuOH and not with PhOH is partly compensated by the reaction of H^\bullet and the carbon-centred radicals produced from the *t*-BuOH. The kinetic curves suggest that *t*- $\bullet\text{BuOH}$ also reacts with PhOH, but the rate constant might be much smaller than that of $\bullet\text{OH} + \text{PhOH}$ reaction. Consequently, this additive may act also as radical transfer compound. This possibility was checked using N_2O saturated solutions. In such solution e_{aq}^- entirely transforms to $\bullet\text{OH}$ (in the reaction $e_{\text{aq}}^- + \text{N}_2\text{O} + \text{H}_2\text{O} \rightarrow \bullet\text{OH} + \text{N}_2 + \text{OH}^-$ (Buxton et al., 1988)), and then to *t*- $\bullet\text{BuOH}$. The observed small decrease in PhOH concentration is attributed to the *t*- $\bullet\text{BuOH} + \text{PhOH}$ reaction. The majority of *t*- $\bullet\text{BuOH}$ probably disappears in radical–radical reactions.

In the presence of dissolved O_2 the reaction of e_{aq}^- with PhOH is hindered by e_{aq}^- reaction with dissolved O_2 , and *t*- $\bullet\text{BuOH}$ undergoes transformation to peroxy radicals (*t*- $\bullet\text{OOBuOH}$). At $1.0 \times 10^{-3} \text{ mol L}^{-1}$ *t*-BuOH concentration the degradation-dose curve is very similar to the curve observed in the absence of *t*-BuOH (Fig. 1b). The high degradation rate is mainly due the high percentage of $\bullet\text{OH}$ reacting with PhOH. However, when the *t*-BuOH concentration is increased to 5.0×10^{-2} or $5.0 \times 10^{-1} \text{ mol L}^{-1}$, the degradation rate of PhOH becomes quite small due to the low percentage of $\bullet\text{OH} + \text{PhOH}$ reaction. *t*- $\bullet\text{OOBuOH}$ is assumed to have low reactivity with PhOH. At $5.0 \times 10^{-1} \text{ mol L}^{-1}$ *t*-BuOH concentration during energy deposition about 4% of the absorbed energy is taken up directly by *t*-BuOH, this effect also slightly decreases the degradation rate of

Table 2
G-values ($\mu\text{mol J}^{-1}$) of PhOH removal under different conditions.

Additive	Concentration of additive (mol L^{-1})	Deoxygenated	Oxygenated
No additive		0.056	0.120
<i>t</i> -BuOH	1.0×10^{-3}	0.042	0.110
	5.0×10^{-2}	0.040	0.020
	5.0×10^{-1}	0.036	0.010
HCOOH	1.0×10^{-3}	0.100	0.120
	5.0×10^{-2}	0.034	0.020
	5.0×10^{-1}	0.010	0.006
HCOO ⁻	1.0×10^{-3}	0.024	0.060
	5.0×10^{-2}	0.010	0.020
	5.0×10^{-1}	0.005	0.010

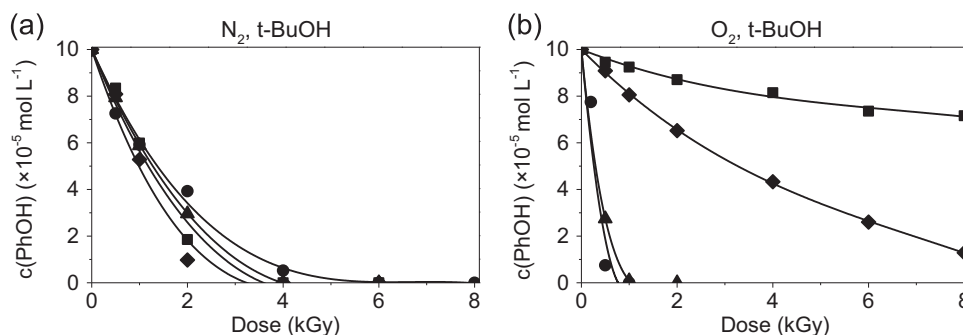


Fig. 1. PhOH concentration versus absorbed doses in the absence (●) and in the presence of *t*-BuOH (▲: 1.0×10^{-3} mol L⁻¹, ◆: 5.0×10^{-2} mol L⁻¹, ■: 5.0×10^{-1} mol L⁻¹) in solutions purged with N₂ (a) or O₂ (b).

PhOH. Moreover, O₂^{•-} formed due to e_{aq}⁻ + O₂ reaction has also minor contribution to the degradation of PhOH.

3.3. Influence of HCOOH

HCOOH reacts with •OH and e_{aq}⁻ with similar rate constants, it also reacts with •H but at one order of magnitude lower rate constant than with the other two primary intermediates (Table 1). The percentage of •OH reacting with PhOH for the three HCOOH concentrations is 87, 11 and 1% calculated by the Eq. (2).

In O₂-free solutions, when 1.0×10^{-3} , 5.0×10^{-2} and 5.0×10^{-1} mol L⁻¹ HCOOH is added into the system the pH decreases from about 6.7 to ~3.5, ~2.6 and ~2. Under these conditions the reaction of e_{aq}⁻ with PhOH is negligible and e_{aq}⁻ reacts with both HCOOH and H₃O⁺, however the reaction with H₃O⁺ dominates (98, 89 and 75%) due to the low pH. The increase of the degradation rate in solution with 1.0×10^{-3} mol L⁻¹ HCOOH (the amount of degraded PhOH has doubled) (Fig. 2a, Table 2) can be attributed to the relatively high contribution of •H to the degradation of PhOH. At this HCOOH concentration besides the •H-initiated transformation of PhOH, the majority of •OH reacts also with PhOH. At 5.0×10^{-2} mol L⁻¹ HCOOH concentration the degradation rate was lower than without the additive. In this solution the majority of •OH reacts with HCOOH which is not compensated by the reaction of •COOH with PhOH. At 5.0×10^{-1} mol L⁻¹ HCOOH concentration the degradation is even slower than in 5.0×10^{-2} mol L⁻¹ HCOOH solution. In this case •OH contribution to PhOH degradation is negligible. PhOH degradation nearly entirely occurs through •H, however at this HCOOH concentration the reaction between HCOOH and •H is also significant (54%). Based on the kinetic curves we assume that •COOH has little contribution to PhOH degradation.

In O₂-saturated solutions HCOOH in every concentration decreased markedly the rate of degradation of PhOH (Fig. 2b). In these cases e_{aq}⁻ reacts primarily with H₃O⁺ (75, 87 and 77%) and results in H•. However, the H• is completely trapped by dissolved

O₂, consequently its reaction with PhOH and HCOOH are successfully hindered. In these cases, both primary radicals are converted to the less reactive HO₂[•]. The extents of degradations in solutions with 5.0×10^{-2} and 5.0×10^{-1} mol L⁻¹ HCOOH, however are much higher than expected based on the percentage of •OH reacting with PhOH. We assume that •COOH, HO₂[•] or the stabilization product of the latter (H₂O₂) may also contribute to the degradation of PhOH.

3.4. Influence of HCOO⁻

The presence of HCOO⁻ reduced the rate of transformation of PhOH markedly both in deoxygenated and in oxygenated solutions (Fig. 3a and b) in all applied concentrations. After 1 kGy absorbed dose the amount of degraded PhOH was less than 5%, using 5.0×10^{-1} mol L⁻¹ HCOONa. The degree of decrease of the degradation rate was more significant in the case of solutions saturated by O₂, than in the O₂-free case.

The pH of HCOONa containing solutions increased continuously from 7 to almost 10 during γ irradiation, probably caused by the reactions of CO₂^{•-} with •OH and which lead to OH⁻ (e_{aq}⁻ + CO₂^{•-} + H₂O → HCO₂⁻ + OH⁻, $k = 9.0 \times 10^9$ L mol⁻¹ s⁻¹ (Schwarz, 1992)). In high pH solutions PhOH was present in its deprotonated form, too, (phenolate ion, PhO⁻; pK_a = 9.88 (Liptak et al., 2002)) incrementing concentrations. The reactivity of PhO⁻ might be lower than that of PhOH towards some of the intermediates, for example PhO⁻ reacts with e_{aq}⁻ at one order of magnitude lower rate constant (Anbar and Neta, 1967) than PhOH.

HCOO⁻ converts •OH and H• into the less reactive carbon-centred radical (CO₂^{•-}) with relatively high reaction rate constants (Table 1). In the presence of HCOO⁻ the percentage of •OH reacting with PhOH is 21, 0.5 and 0.05% at 1.0×10^{-3} , 5.0×10^{-2} and 5.0×10^{-1} mol L⁻¹ HCOO⁻ concentrations, respectively, calculated by Eq. (2). This means that the decomposition of PhOH at higher HCOO⁻ concentration cannot be induced by •OH reaction. The rate of reaction of this additive with e_{aq}⁻ is low considering

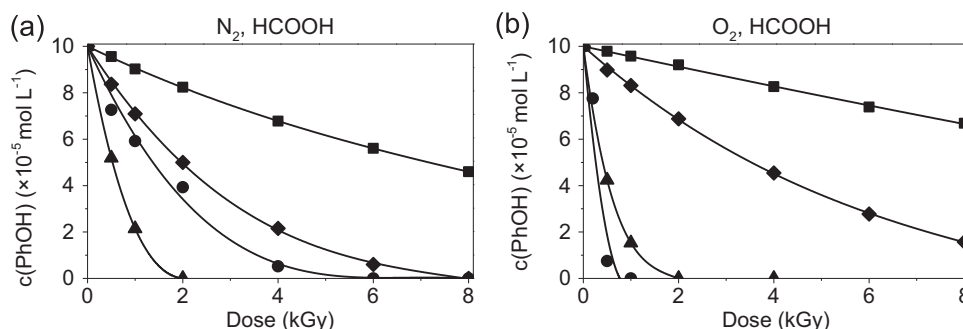


Fig. 2. PhOH concentration versus absorbed doses in the absence (●) and in the presence of HCOOH (▲: 1.0×10^{-3} mol L⁻¹, ◆: 5.0×10^{-2} mol L⁻¹, ■: 5.0×10^{-1} mol L⁻¹) in solutions purged with N₂ (a) or O₂ (b).

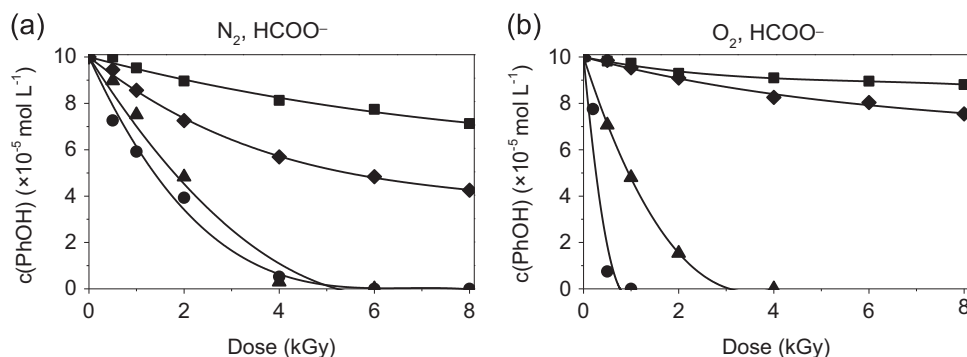


Fig. 3. PhOH concentration versus absorbed doses in the absence (●) and in the presence of HCOO^- (▲: $1.0 \times 10^{-3} \text{ mol L}^{-1}$, ◆: $5.0 \times 10^{-2} \text{ mol L}^{-1}$, ■: $5.0 \times 10^{-1} \text{ mol L}^{-1}$) in solutions purged with N_2 (a) or O_2 (b).

the rate constant, therefore, in deoxygenated solutions e_{aq}^- can be considered as the predominant species throughout the irradiation. However, based on the degradation rates the contribution of e_{aq}^- to the transformation of PhO^-/PhOH was likely to be minor.

In the presence of both O_2 and HCOO^- , $\text{CO}_2^{\bullet -}$ and e_{aq}^- reacts almost exclusively with dissolved O_2 , and the total radical set was converted to $\text{O}_2^{\bullet -}$. It means that this radical anion was the only one that could contribute in enhanced concentration to the transformation process. However, it has very low reactivity towards PhOH thus the transformation rates of PhOH were also low. On the other hand, the participation of carbon-centred radicals formed ($\text{CO}_2^{\bullet -}$) to the degradation of PhO^-/PhOH might be also minor. Thus, the results suggest that HCOONa (and HCOOH also) can be considered as radical scavenger material as well.

4. Summary

t-BuOH as radical scavenger and HCOOH and HCOO^- as radical transfer materials were applied in three concentrations to investigate their influences on the rate of PhOH transformation in γ -irradiated, deoxygenated and O_2 -saturated solutions. The dissolved O_2 increased significantly the PhOH transformation rate. In oxygenated solutions the radical that forms in $\bullet\text{OH} + \text{PhOH}$ reaction transforms to peroxy radical, whereas e_{aq}^- and $\bullet\text{H}$ transform to the $\text{O}_2^{\bullet -}$ and HO_2^{\bullet} and $\bullet\text{OH}$ concentration increases.

The radical transfer or scavenger materials applied reduced the rate of PhOH transformation by a similar degree in oxygenated solutions. The explanation of this phenomenon might be that the simultaneous presence of two radical transfer materials (O_2 and the organic additives) in excess proportionally to PhOH converted the total radical set to the less reactive HO_2^{\bullet} or $\text{O}_2^{\bullet -}$. These species merely made minor contributions to the transformation of PhOH even in elevated concentrations.

Under deoxygenated reaction conditions, *t*-BuOH did not affect significantly the degradation rate of PhOH. HCOOH in $1.0 \times 10^{-3} \text{ mol L}^{-1}$ concentration not reduced, but promoted the degradation. On the other hand, HCOO^- in every concentration reduced the rate of PhOH degradation. At $1.0 \times 10^{-3} \text{ mol L}^{-1}$ additive concentration the percentages of the reaction of $\bullet\text{OH}$ with PhOH are correlated with the *G*-values of PhOH degradation. This result suggests that in this concentration $\bullet\text{OH}$ is the most relevant reactant towards PhOH. Moreover, it is an interesting result that these additives in tenfold concentration compared to the target substance had relatively small effect on the degradation of PhOH in deoxygenated conditions. However, using higher additive concentrations, their competitive reactions for the primary intermediates came into prominence, thus they highly reduced the efficiency of PhOH decomposition.

The presented results showed that HO_2^{\bullet} and $\text{O}_2^{\bullet -}$ and also the

carbon-centred radicals formed have only a minor contribution to the degradation of PhOH. The difference between the kinetic curves observed in the presence of the various additives in O_2 -saturated solutions suggests a reactivity relation $t\text{-}\bullet\text{BuOH} > \bullet\text{COOH} > \text{CO}_2^{\bullet -}$ for the carbon-centred radicals.

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