New insights regarding the impact of radical transfer and scavenger materials on the •OH-initiated phototransformation of phenol

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ABSTRACT

For the investigations of the oxidative transformations of various organic substances knowledge of the roles and relative contributions of the reactive species formed to the transformations of the target substances is needed. The vacuum ultraviolet (172 nm) photolysis of aqueous solution of phenol (PhOH) $(1.0 \times 10^{-4}\,mol\,L^{-1})$ as model compound was therefore investigated in this work in the presence or absence of various radical scavenger (tert-butanol, t-BuOH) and transfer materials (dissolved O_2; formic acid, HCOOH; sodium formate, HCOONa).

It was concluded that the rate of degradation of PhOH increased significantly (up to 3-fold) in the presence of dissolved O_2 mainly because of the hindered recombination of the primary radicals (H• and •OH), the increased concentration of •OH.

All of the applied organic radical scavenger and radical transfer materials decreased the initial rate of degradation of PhOH mainly by reducing the concentrations of reactive primary radicals. In O_2-free solutions, the effects of HCOOH and formate anion (HCOO$^-$) were found to be more significant than that of t-BuOH, which can be explained by the different reactivities of the carbon-centred radicals formed. In O_2 saturated solutions, there was no significant difference between the initial rates of transformation determined in the presence of the various additives. In these cases, the less reactive HO$_2$• or O$_2$•$^-$ were the most significant species of the radical set, and it seems that these radicals make only minor contributions to the transformation of PhOH, they contribute mainly to the formation of H_2O_2 instead.

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1. Introduction

Various pollutants, such as medicinal agents and pesticides, may possibly enter the environment, accumulate in living organisms and cause serious environmental problems. These contaminants cannot usually be completely removed by means of conventional water treatment methods, which therefore have to be supplemented, for example, with advanced oxidation processes (AOPs), which are generally based on radical-initiated reactions.

Most AOPs depend on the formation of hydroxyl radicals (•OH), which are very reactive, non-selective oxidizing species capable to initiate the oxidative transformation of extensive variety of organic pollutants [1]. One such AOP is the vacuum ultraviolet (VUV) process, which involves reactions initiated by high-energy photons generated by VUV lamps emitting radiation at wavelengths shorter than 200 nm. One type of VUV lamp is the excimer lamp, which emits quasi-monochromatic radiation whose wavelength depends on the type of gas applied [2]. Although the efficiency and mechanisms of the VUV process have been studied by several researchers [3–7], further investigations may present challenges due to the nature of the system. More than 30 reactions are known to occur only during the VUV photolysis of pure liquid H_2O [8], involving several radical species (•OH; hydrogen radical, •H; hydrated electrons, e$_{aq}^-$; hydroperoxyl radical/superoxide radical

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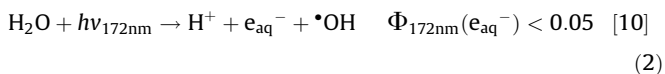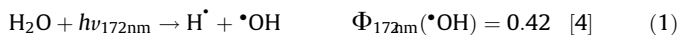E-mail addresses: kozmerzs@chem.u-szeged.hu (Zs. Kozmér), arany.eszter@chem.u-szeged.hu (E. Arany), alapi@chem.u-szeged.hu (T. Alapi), rozsa.georgina@chem.u-szeged.hu (G. Rózsa), hernadi@chem.u-szeged.hu (K. Hernádi), dombia@chem.u-szeged.hu (A. Dombi).
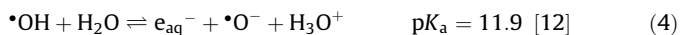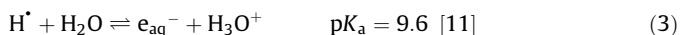
anion, $HO_2^\bullet/O_2^{\bullet-}$ etc.) which can react with each other or with other species in the system, such as organic molecules or dissolved O_2. Understanding of the roles and relative contributions of these species to the transformation of organic substances is one of the keys to optimization of the VUV process and other AOPs.

In the course of the VUV photolysis of aqueous solutions, VUV photons induce homolytic dissociation of H_2O molecules [9]. When a xenon excimer lamp is used, which emits 172 nm VUV light, the initiation processes are [4,10]:

$$H_2O + h\nu_{172nm} \rightarrow H^\bullet + {}^\bullet OH \qquad \Phi_{172nm}({}^\bullet OH) = 0.42 \quad [4] \qquad (1)$$

$$H_2O + h\nu_{172nm} \rightarrow H^+ + e_{aq}^- + {}^\bullet OH \qquad \Phi_{172nm}(e_{aq}^-) < 0.05 \quad [10] \qquad (2)$$

${}^\bullet OH$, $H^\bullet$ and (in lower yield) e_{aq}^- are generated as primary radicals during the VUV photolysis of aqueous solutions. Since e_{aq}^- is present in very low concentration during VUV photolysis, its reactions are generally not taken into consideration.

${}^\bullet OH$ and $H^\bullet$ can dissociate at basic pH, regarding their acid dissociation constants [11,12]:

$$H^\bullet + H_2O \rightleftharpoons e_{aq}^- + H_3O^+ \qquad pK_a = 9.6 \quad [11] \qquad (3)$$

$${}^\bullet OH + H_2O \rightleftharpoons e_{aq}^- + {}^\bullet O^- + H_3O^+ \qquad pK_a = 11.9 \quad [12] \qquad (4)$$

The primary radicals are presumably formed in a solvent cage. In this case, H_2O molecules act as the 'cage' and prevent the species from breaking through the first solvation shell. When the system contains O_2 and/or organic molecules, competition generally occurs between the recombination of primary radicals and their reactions with these substances [7].

In the presence of O_2 the previously mentioned primary radicals are accompanied by other reactive oxygen species (ROS), such as $HO_2^\bullet$ [12]:
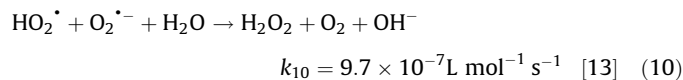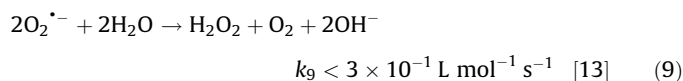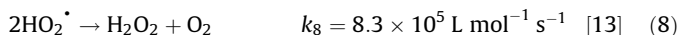
$$H^\bullet + H_2O \rightleftharpoons HO_2^\bullet \qquad k_5 = 2.1 \times 10^{10} \text{ L mol}^{-1}\text{ s}^{-1} \quad [12] \qquad (5)$$
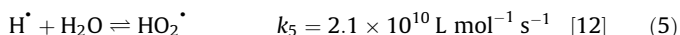
The species $HO_2^\bullet$ and $O_2^{\bullet-}$ form a conjugate acid–base pair, the ratio of their concentration depends on the current pH [13].

$$HO_2^\bullet + H_2O \rightleftharpoons O_2^{\bullet-} + H_3O^+ \qquad pK_a = 4.8 \quad [13] \qquad (6)$$

Although the recombination of ${}^\bullet OH$ theoretically results in the formation of hydrogen peroxide (H_2O_2) (Eq. (7)), this reaction takes place to only a minor extent in consequence of the other competing reactions of ${}^\bullet OH$ (e.g. its reactions with $H^\bullet$ or organic substances), resulting in a minor or negligible H_2O_2 concentration under deoxygenated conditions [12,14–16].

$$2\,{}^\bullet OH \rightarrow H_2O_2 \qquad k_7 = 5.5 \times 10^9 \text{ L mol}^{-1}\text{ s}^{-1} \quad [12] \qquad (7)$$
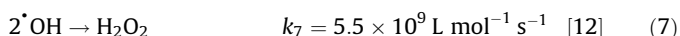
H_2O_2 is mainly formed in the disproportionation of $HO_2^\bullet$ and $O_2^{\bullet-}$ [13]:

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \qquad k_8 = 8.3 \times 10^5 \text{ L mol}^{-1}\text{ s}^{-1} \quad [13] \qquad (8)$$

$$2O_2^{\bullet-} + 2H_2O \rightarrow H_2O_2 + O_2 + 2OH^- \qquad k_9 < 3 \times 10^{-1} \text{ L mol}^{-1}\text{ s}^{-1} \quad [13] \qquad (9)$$

$$HO_2^\bullet + O_2^{\bullet-} + H_2O \rightarrow H_2O_2 + O_2 + OH^- \qquad k_{10} = 9.7 \times 10^{-7}\text{L mol}^{-1}\text{ s}^{-1} \quad [13] \qquad (10)$$
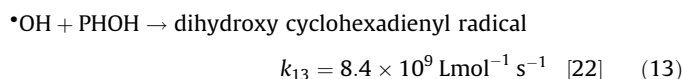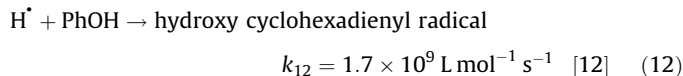
The experimentally observed rate of the disproportionation of $HO_2^\bullet/O_2^{\bullet-}$ is dependent on the pH [13]. The concentration of H_2O_2 formed can therefore give information about the concentrations of ROS (mainly $HO_2^\bullet/O_2^{\bullet-}$). On the other hand, the formation of both $HO_2^\bullet$ and $O_2^{\bullet-}$ is also possible, due to the further transformation of organic peroxyl radicals formed in the reactions of the primary radicals with organic compounds in the presence of molecular O_2 [17,18].

Radical-based reactions of the model compounds in VUV-irradiated aqueous solutions can be investigated by the use of various radical scavenger and/or radical transfer materials. When such additional compounds are also present, they compete with the model molecules for the primary radicals, which generally results in a lower rate of transformation of the model molecule. The further transformations of the radicals or radical ions formed in the reactions of the additional compound with primary radicals can result in species which can open further, new reaction pathways or shift the ratios of the existing ones for the transformation of the model compound [17,19,20]. These additional compounds are called radical transfer materials. The additional compound is referred to as a radical scavenger when its further transformation does not result in the formation of other reactive species.

As mentioned previously, dissolved O_2 affects the concentrations of primary radicals, since O_2 reacts with $H^\bullet$ and converts it to $HO_2^\bullet$ (Eq. (5)). Additionally, it can form peroxyl radicals by addition to carbon-centred radicals [17,21]. On the other hand, in the absence of dissolved O_2, $H^\bullet$ combines to yield molecular H_2 which, due to its low solubility in aqueous systems, is assumed to be of little importance within the manifold of reactions of oxygenated intermediates [8].

$$2H^\bullet \rightarrow H_2 \qquad k_{11} = 1.0 \times 10^{10} \text{ L mol}^{-1}\text{ s}^{-1} \quad [8] \qquad (11)$$
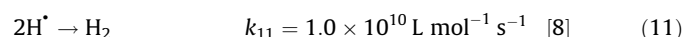
In this study the phenol (PhOH) was chosen as model compound to investigate the role and contribution of various reactive species to the transformation in the VUV irradiated aqueous solution. Both of the primary radicals produced during VUV photolysis react with PhOH with reaction rate constants of the same order of magnitude [12,22]:

$$H^\bullet + PhOH \rightarrow \text{hydroxy cyclohexadienyl radical}$$
$$k_{12} = 1.7 \times 10^9 \text{ L mol}^{-1}\text{ s}^{-1} \quad [12] \qquad (12)$$

$${}^\bullet OH + PHOH \rightarrow \text{dihydroxy cyclohexadienyl radical}$$
$$k_{13} = 8.4 \times 10^9 \text{ Lmol}^{-1}\text{ s}^{-1} \quad [22] \qquad (13)$$

The transformation of PhOH can be initiated by the addition of ${}^\bullet OH$ to the aromatic ring in the ortho (48%) or para (36%) position. Addition to the meta or ipso position is expected to be quite negligible [23]. In the presence of dissolved O_2, further transformations of dihydroxycyclohexadienyl radicals result in mainly 1,2- (Eq. (14)) or 1,4-dihydroxyphenols (Eq. (15)) via $HO_2^\bullet$ elimination [21,23].
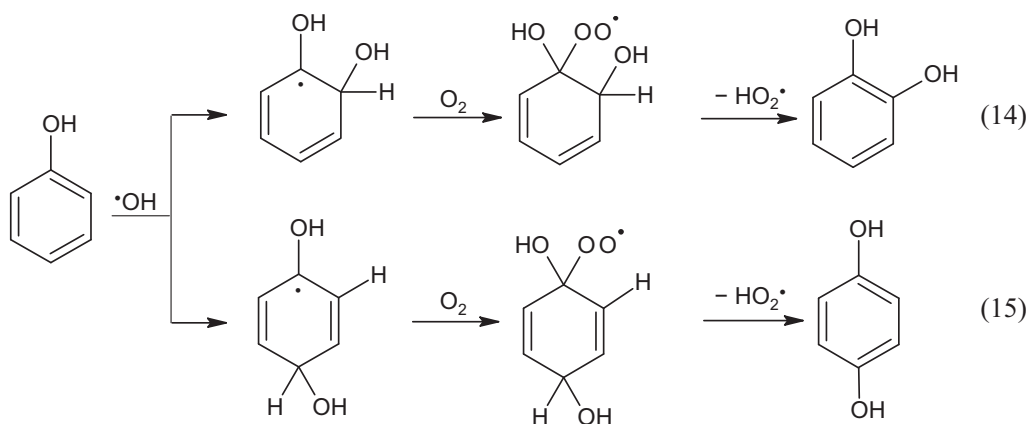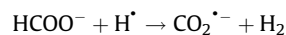
In O_2-free solutions the most likely further transformation of the cyclohexadienyl radicals is their recombination and dismutation [8] and various ring-opening reactions [24].

Tert-butanol (*t*-BuOH) is a $^\bullet$OH scavenger. It reacts with $^\bullet$OH with a high rate constant (k_{16}) [12], and with H$^\bullet$ with a 3 orders of magnitude lower rate constant (k_{17}) [26]. Consequently, the concentration of H$^\bullet$ may remain significant, whereas the concentration of reactive $^\bullet$OH must be low in solutions containing *t*-BuOH.

H-abstraction from *t*-BuOH yields 2,2-dimethyl-2-hydroxyethyl radical (*t*-$^\bullet$BuOH), which has low reactivity towards organic compounds [25].
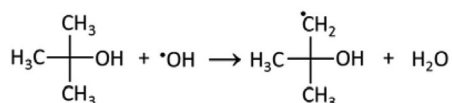

$$k_{16} = 6.0 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1} \text{ [12] (16)}$$

$$k_{17} = 1.7 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1} \text{ [26] (17)}$$

Formic acid (HCOOH) and formate anion (HCOO$^-$) react with $^\bullet$OH (Eqs. (19) and (21)) and H$^\bullet$ (Eqs. (20) and (22)) and result in carbon-centred radicals of low reactivity, thus these compounds behave as radical transfer materials [21,27,12].

$$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+ \qquad pK_a = 3.75 \quad [27] \qquad (18)$$

$$HCOOH + {}^\bullet OH \rightarrow {}^\bullet COOH + H_2O$$
$$k_{19} = 1.3 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1} \quad [12] \qquad (19)$$

$$HCOOH + H^\bullet \rightarrow {}^\bullet COOH + H_2$$
$$k_{20} = 4.4 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1} \quad [12] \qquad (20)$$

$$HCOO^- + {}^\bullet OH \rightarrow CO_2^{\bullet -} + H_2O$$
$$k_{21} = 3.2 \times 10^5 \text{ Lmol}^{-1} \text{ s}^{-1} \quad [12] \qquad (21)$$

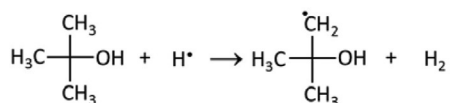$$HCOO^- + H^\bullet \rightarrow CO_2^{\bullet -} + H_2$$
$$k_{22} = 2.1 \times 10^8 \text{ Lmol}^{-1} \text{ s}^{-1} \quad [12] \qquad (22)$$

The carboxyl radicals ($^\bullet$COOH) and carboxyl radical anions ($CO_2^{\bullet -}$) form a conjugate acid–base pair [27]:
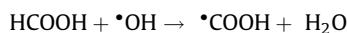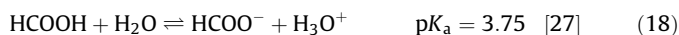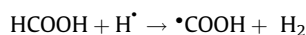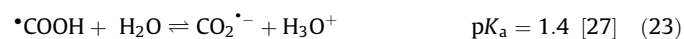
$$^\bullet COOH + H_2O \rightleftharpoons CO_2^{\bullet -} + H_3O^+ \qquad pK_a = 1.4 \text{ [27]} \quad (23)$$

In the presence of O_2, $^\bullet$COOH and $CO_2^{\bullet -}$ undergo transformation to $HO_2^\bullet$ and $O_2^{\bullet -}$, respectively [27,28]:
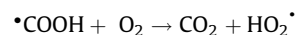
$$^\bullet COOH + O_2 \rightarrow CO_2 + HO_2^\bullet$$
$$k_{24} = 3 \times 10^9 \text{ Lmol}^{-1} \text{ s}^{-1} \quad [27] \qquad (24)$$
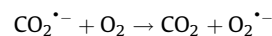
$$CO_2^{\bullet -} + O_2 \rightarrow CO_2 + O_2^{\bullet -}$$
$$k_{25} = 4.2 \times 10^9 \text{ Lmol}^{-1} \text{ s}^{-1} \quad [28] \qquad (25)$$

For optimization of the transformation pathways of organic substances, accurate knowledge of the mechanisms is needed. Only limited knowledge is available concerning the effects of various radical scavenger and transfer materials on the radical set generated during AOPs. The aim of this work was to investigate the effects of dissolved O_2 and the influences of *t*-BuOH as $^\bullet$OH

scavenger, and HCOOH and HCOO$^-$ as $^\bullet$OH transfer materials on the VUV degradation process of PhOH. Comparison of the results obtained on the use of HCOOH (pH 1.9) and HCOO$^-$ (pH 8.0), the effects of pH were also investigated.

2. Material and methods

2.1. The experimental setup

250 mL 1.0×10^{-4} mol L^{-1} (c_0) aqueous PhOH (VWR, 100.0%) solution prepared in ultrapure MILLI-Q H$_2$O (MILLIPORE Milli-Q Direct 8/16, permeate conductivity: 13.3 μS cm^{-1}, resistivity: 18.2 MΩ cm, total organic carbon (TOC) content: 2 ppb) was irradiated with VUV light produced by a Xe excimer lamp. The solution was circulated between the thermostated (25 $\pm$ 0.5 °C) reactor and reservoir by a Heidolph Pumpdrive 5001 peristaltic pump at a flow rate of 375 mL min^{-1}. During irradiation, the pH and the concentrations of H$_2$O$_2$ and PhOH were measured. The kinetic measurements were started by switching on the lamp.

The Xe excimer lamp (Radium Xeradex^{TM}, length: 130 mm, external diameter: 40 mm, 20 W electrical input power) emitted quasi-monochromatic VUV photons at 172 $\pm$ 14 nm (7.21 eV). The photon flux of the light source determined by means of methanol actinometry [3] was found to be $(3.0 \pm 0.1) \times 10^{-6}$ mol$_{photon}$ s^{-1}. The lamp was placed into the centre of a triple-walled tubular glass reactor (length: 220 mm, external diameter: 70 mm, the inner wall being made of Suprasil$^{\textregistered}$ quartz). The irradiated solution was circulated within the two inner walls of the reactor in a 2.0 mm thick layer.

2.2. Materials

To investigate the effect of dissolved O$_2$, either N$_2$ (Messer, >99.99% purity) or O$_2$ (Messer, >99.99% purity, resulting in a dissolved O$_2$ concentration of 12.5×10^{-4} mol L^{-1}) was bubbled through the solutions at a flow rate of 600 mL min^{-1}. The injection of the gas was started 30 or 15 min before each experiment in the cases of N$_2$ and O$_2$, respectively, and was continued throughout the irradiation.

The samples contained 0.50 mol L^{-1} t-BuOH (VWR, 100.0%), HCOOH (VWR, 99.0%) or sodium formate (HCOONa, FLUKA, 99.0%). The concentration of the additives was 5000 times higher than the c_0 of PhOH (1.0×10^{-4} mol L^{-1}) so as to ensure that the majority of the primary radicals reacted with the organic radical scavenger or transfer materials.

For the investigation of the effect of the basic pH on the VUV transformation of PhOH, NaOH (VWR, 99% purity) was added to the solutions to adjust the initial pH in the range of 7–11.

2.3. Analytical methods

The H$_2$O$_2$ concentration was measured spectrophotometrically by using the Hydrogen Peroxide Test by Merck, valid in the range 4.41×10^{-7}–1.76×10^{-4} mol L^{-1}. The method is based on the reduction of Cu^{II}-dimethylphenanthroline by H$_2$O$_2$ to result in a coloured Cu^{I} ion-containing complex ($\varepsilon_{454\,nm}$ = 14,300 $\pm$ 200 L mol^{-1} cm^{-1} [29]). The absorbance of the sample was measured at 455 nm in cells with a path-length of 1.00 cm, using an Agilent 8453 diode array spectrophotometer. The pH of the sample must be between 4 and 10 for measurement of its H$_2$O$_2$ concentration; when necessary, it was therefore adjusted with HCl (VWR, diluted from 36.0% solution) or NaOH (VWR, 99% purity). Analysis was performed with a Consort C835 S/N 74117 pH-meter.

The concentration of PhOH was followed by an Agilent 1100 Series high-performance liquid chromatograph with UV detection. Aromatic compounds were separated on an RP-18 column (LiChroCART$^{\textregistered}$ 150-4.6, 5 μm particle size), using 35% methanol (VWR, 99.80%) and 65% ultrapure MILLI-Q H$_2$O as eluent at a flow rate of 0.8 mL min^{-1} at 25 °C. In each case, 20 μL of sample was analysed. The wavelength for UV detection was 210 nm. The decomposition of PhOH was characterized by the initial rate of transformation, which was obtained from linear regression fits to the curves of the actual concentration of PhOH versus the time of irradiation, up to 10% of the concentration of transformed PhOH.

During the degradation processes, the pH usually changes, and it was therefore measured at 5 min intervals with an inoLab pH 730p pH-meter.

The standard deviations of the measured PhOH and H$_2$O$_2$ concentrations and pH values are presented in the figures.

3. Results and discussion

3.1. Effects of dissolved O$_2$

O$_2$ is one of the most important radical transfer materials, which reacts with H$^\bullet$ and converts it to less reactive HO$_2$$^\bullet$ (Eq. (5)).

The rate of the transformation of PhOH was significantly higher in O$_2$-saturated solutions (Table 1) than under O$_2$-free conditions (Fig. 1a), which can be explained mainly by the addition of molecular O$_2$ to the formed radical in the first, reversible step of PhOH with $^\bullet$OH (Eqs. (14) and (15)). With regard to the rate constants of H$^\bullet$ with O$_2$ and PhOH (k_5 and k_{12}), and since the concentration of dissolved O$_2$ ($c_{O2} = 1.25 \times 10^{-3}$ mol L^{-1}) was one order of magnitude higher than the initial concentration of PhOH ($c_0 = 1.0 \times 10^{-4}$ mol L^{-1}), H$^\bullet$ reacted mainly with O$_2$ (Eq. (5)). The effect of the suppressed concentration of H$^\bullet$ on the rate of transformation of PhOH could be greatly overcompensated by the effect of the higher concentrations of $^\bullet$OH. The hindered recombination of the primary radicals might also contribute to the higher rate of transformation of PhOH in oxygenated, as compared with deoxygenated solutions.

In the absence of O$_2$ the dihydroxy-cyclohexadienyl radicals might disproportionate to yield PhOH and dihydroxybenzene [8]. In oxygenated solutions, the addition of O$_2$ to these radicals competes with the dismutation reaction, and thus hinders the regeneration of PhOH [30]. Consequently, this process might also contribute to the increased transformation rate of PhOH measured in the presence of dissolved O$_2$.

Table 1
Initial rates of transformation of PhOH (r_0) and the most significant species of the presumed radical set.

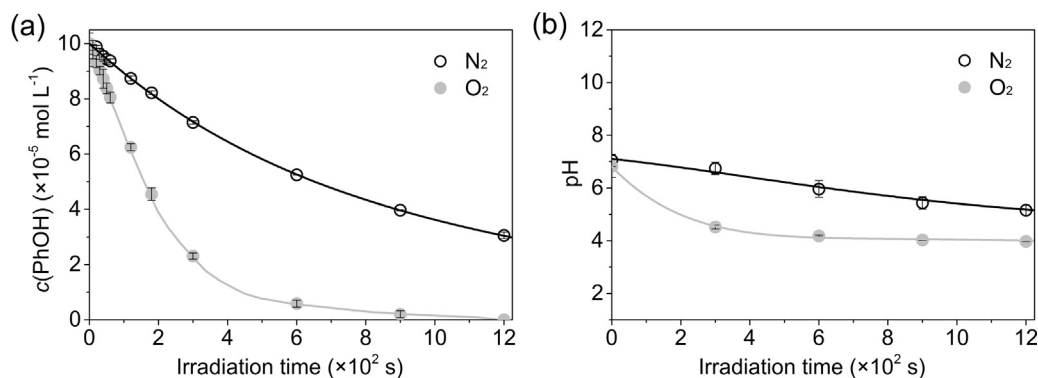|	No additive	t-BuOH	HCOOH	HCOO$^-$
Injected gas	N$_2$			
r_0 ($\times 10^{-8}$ mol L^{-1} s^{-1})	12 $\pm$ 1	5.7 $\pm$ 0.3	3.2 $\pm$ 0.1	3.1 $\pm$ 0.3
Radical set	$^\bullet$OH $\approx$ H$^\bullet$	H$^\bullet$ $\ll$ t-$^\bullet$BuOH	H$^\bullet$ $\ll$ $^\bullet$COOH	H$^\bullet$ $\ll$ CO$_2$$^{\bullet-}$
Injected gas	O$_2$			
r_0 ($\times 10^{-8}$ mol L^{-1} s^{-1})	33 $\pm$ 1	6.2 $\pm$ 0.5	7.5 $\pm$ 0.4	6.1 $\pm$ 0.6
Radical set	$^\bullet$OH, HO$_2$$^\bullet$ $\ll$ O$_2$$^{\bullet-}$	HO$_2$$^\bullet$ $\ll$ O$_2$$^{\bullet-}$	HO$_2$$^\bullet$	O$_2$$^{\bullet-}$

Fig. 1. PhOH concentration (a) and pH (b) versus irradiation time in the absence and in the presence of O_2.
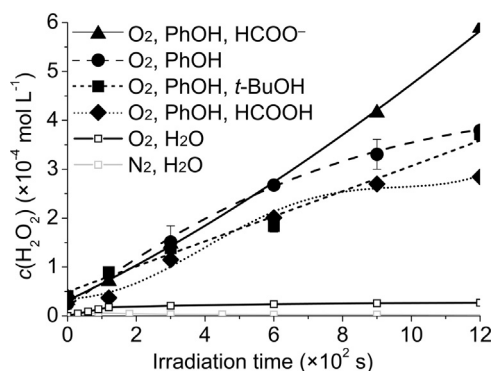

Fig. 2. H_2O_2 concentration versus irradiation time in the absence and in the presence of $1.0 \times 10^{-4}\,\text{mol}\,\text{L}^{-1}$ PhOH and $5.0 \times 10^{-1}\,\text{mol}\,\text{L}^{-1}$ t-BuOH, HCOOH or $HCOO^-$ in solutions purged with N_2 or O_2.

The reaction rate constants of $HO_2^\bullet$ and $O_2^{\bullet-}$ with PhOH (k (PhOH + $HO_2^\bullet$) = $2.7 \times 10^3\,\text{L}\,\text{mol}^{-1}\,\text{s}^{-1}$ [31], k(PhOH + $O_2^{\bullet-}$) = $5.8 \times 10^2\,\text{L}\,\text{mol}^{-1}\,\text{s}^{-1}$ [32]) are much lower than the rate constant of reaction of PhOH with $^\bullet$OH (k_{13}). This means that the contribution of these species to the transformation of PhOH is negligible, and the reaction with $^\bullet$OH must be the significant process.

During the VUV photolytic transformation of PhOH, the pH of the solutions decreased from 7 to 4 after a relatively short period of irradiation (the conversion of PhOH being 80%) in solutions saturated with O_2 (Fig. 1b). The explanation of this acidification is probably the formation of various aliphatic organic acids formed by the ring-opening reactions from PhOH, aromatic intermediates and the further fragmentations [5]. Under O_2-free conditions, the pH decreased only slightly.

In pure H_2O (in the absence of both dissolved O_2 and organic substances), the recombination of the primary radicals ($^\bullet$OH and $H^\bullet$) is very favourable because of the 'cage effect' [33,34]. Consequently, the recombination of $^\bullet$OH radicals (k_7) and therefore the concentration of H_2O_2 was negligible (Fig. 2) in the absence of O_2, in accordance with the literature. This confirmed that without dissolved O_2 the concentration of primary radicals in pure H_2O is very low. On the other hand, the concentration of H_2O_2 in O_2-saturated H_2O was found to be significantly higher (it reached $2.5 \times 10^{-5}\,\text{mol}\,\text{L}^{-1}$). In this case, dissolved O_2 reacts with $H^\bullet$ and converts it into $HO_2^\bullet$ (Eq. (5)), which results in higher concentrations of both $^\bullet$OH and $HO_2^\bullet$. It may be the reason for the enhanced concentration of H_2O_2, since the further reactions of

$HO_2^\bullet$ and its deprotonated form $O_2^{\bullet-}$ (k_8–k_{10}) also result in the formation of H_2O_2, as described previously.

In O_2-saturated solutions, the presence of PhOH and other organic substances (t-BuOH, HCOOH or HCOONa) strongly increased the concentration of H_2O_2. The recombination of $^\bullet$OH was significantly suppressed also in these cases. However, the concentrations of $HO_2^\bullet/O_2^{\bullet-}$ were likely to be high since they can be formed in elimination reactions from organic peroxyl radicals [21,28] and due to the addition of O_2 to $H^\bullet$ (Eq. (5)). As concerns the pH, the molar ratio $HO_2^\bullet/O_2^{\bullet-}$ was less than 0.1 until a maximum of 10% PhOH was decomposed, but further acidification of the solution increased the molar ratio $HO_2^\bullet/O_2^{\bullet-}$. Since the reaction rate constants of $HO_2^\bullet$ and $O_2^{\bullet-}$ with organic substances are much lower than those of their reactions with each other (Eqs. (8) and (10)), their further transformations result mainly in H_2O_2 formation. In O_2-free solutions, the H_2O_2 concentration was negligible because of the lack of $HO_2^\bullet/O_2^{\bullet-}$.

3.2. Effects of t-BuOH

t-BuOH as $^\bullet$OH scavenger reacts with $^\bullet$OH with a high rate constant (k_{16}), and with $H^\bullet$ with a 3 orders of magnitude lower rate constant (k_{17}). Consequently, the concentration of $H^\bullet$ may remain significant in the solution that contains t-BuOH. Thus, in O_2-free solutions containing t-BuOH, the transformation of PhOH can be induced mainly by the reaction with $H^\bullet$ [8], which is at relatively low concentration due to the large excess of t-BuOH. On the other hand, t-$^\bullet$BuOH may have minor contribution to the transformation of PhOH in this case.

In solutions saturated with O_2, t-$^\bullet$BuOH undergoes transformation to the respective peroxyl radical (t-$^\bullet$OOBuOH) (k(t-$^\bullet$BuOH + O_2) = $1.4 \times 10^9\,\text{mol}^{-1}\,\text{L}\,\text{s}^{-1}$ [35]) which also displays negligible reactivity towards PhOH [21,36]. The predominant decay routes of t-$^\bullet$OOBuOH do not give rise to $O_2^{\bullet-}$ [37]. Thus, t-BuOH also acts as an effective radical scavenger in the presence of O_2, though with a small radical-transferring contribution.

The addition of t-BuOH reduced the rate of transformation of PhOH significantly, to a similar value in O_2-free and in O_2-saturated solutions (Table 1) (Fig. 3a). One possible explanation of this phenomenon might be that the concentration of $^\bullet$OH decreases to nearly the same value in both cases, because of the large excess of t-BuOH. In O_2-saturated solutions, $H^\bullet$ is converted to $HO_2^\bullet$, which is present mainly in deprotonated form ($O_2^{\bullet-}$), in view of the pH of the solution. The pH of the solutions containing t-BuOH changed similarly as in the experiments without this additive, both in O_2-free and in O_2-saturated solutions (Fig. 3b). Thus, the pH-dependent ratio $HO_2^\bullet/O_2^{\bullet-}$ should also be similar, $O_2^{\bullet-}$ being the
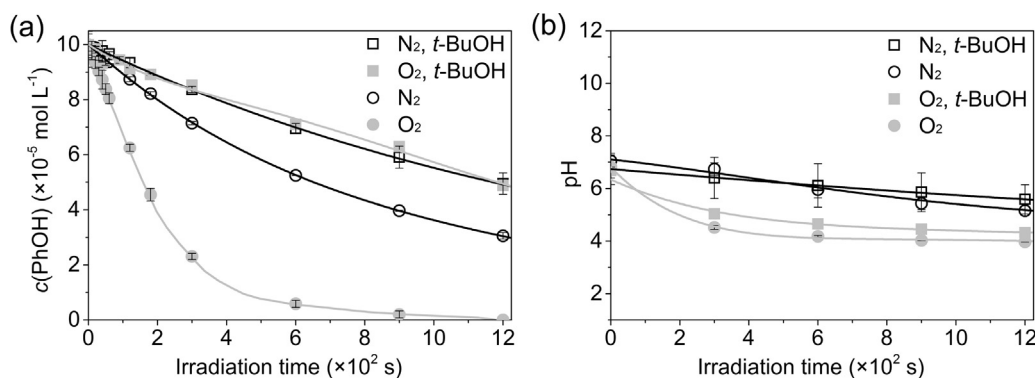
Fig. 3. PhOH concentration (a) and pH (b) versus irradiation time in the absence and in the presence of *t*-BuOH in solutions purged with N_2 or O_2.

predominant species at the beginning of irradiation in both cases, and further decrease of the pH increasing the concentration of $HO_2^\bullet$. The transformation of PhOH can therefore be induced mainly by $HO_2^\bullet/O_2^{\bullet-}$, with very low reactivity towards PhOH [17,18,31,32,38].

- On the other hand, these results suggest that the contribution of the higher concentration of the less reactive $O_2^{\bullet-}$ to the degradation of PhOH in solutions saturated with O_2 is commensurable with the relatively low concentration of $H^\bullet$ in O_2-free solutions. Consequently, $O_2^{\bullet-}$ in elevated concentration may contribute to the decomposition of PhOH. Additionally, it seems that the low (but measurable) reactivity of t-$^\bullet BuOH$ and t-$^\bullet OOBuOH$ towards PhOH is nearly the same.

3.3. Effects of HCOOH

HCOOH is a weak acid and its reactions with $^\bullet OH$ and $H^\bullet$ result in less reactive $^\bullet COOH$ (Eqs. (19) and (20)). In the presence of O_2, this carbon-centred radical undergo transformation to $HO_2^\bullet$ (Eq. (24)).

Under O_2-free conditions, HCOOH reduced the rate of degradation PhOH significantly (Table 1) (Fig. 4a) because it operated as a $^\bullet OH$ scavenger similarly to t-BuOH. Whereas the reaction rate constants of HCOOH and t-BuOH with $^\bullet OH$ (k_{19} and k_{16}) and $H^\bullet$ (k_{20} and k_{17}) have similar values (the same order of magnitude), the effect of HCOOH was more significant than that of t-BuOH, possibly because the reactivity of t-$^\bullet BuOH$ towards PhOH might be higher than that of $^\bullet COOH$. However, the contribution of

the carbon-centred radicals to the transformation of PhOH should be minor.

In O_2-saturated solutions, both primary radicals are converted to the less reactive $HO_2^\bullet/O_2^{\bullet-}$. The pH of the solutions containing HCOOH was ~2 and did not change during the photolysis (Fig. 4b); in this case, therefore only $HO_2^\bullet$ was present in the solutions. The total radical set was therefore converted to $HO_2^\bullet$, meaning that this radical was the only one that could contribute in elevated concentration to the transformation process. The relatively high concentration of this less reactive oxygen species is therefore most probably responsible for the higher initial rate of PhOH transformation in O_2-saturated than in O_2-free solutions.

3.4. Effects of HCOO⁻

The addition of HCOO⁻ induces a basic pH due to the hydrolysis of this anion and converts the reactive $^\bullet OH$ and $H^\bullet$ into less reactive $CO_2^{\bullet-}$ with relatively high reaction rate constants (Eqs. (21) and (22)). As described previously, in the presence of O_2 $CO_2^{\bullet-}$ is converted to $O_2^{\bullet-}$ (Eq. (25)).

In O_2-free solutions, the addition of HCOO⁻ reduced the initial rate of transformation of PhOH to a similar value as for HCOOH (Figs. 4 a and 5a). The effects of HCOO⁻ and HCOOH were more marked than that of t-BuOH. The difference can be explained by the differences in reactivity of the carbon-centred radicals formed, $CO_2^{\bullet-}$, $^\bullet COOH$ and t-$^\bullet BuOH$, respectively.

As the insert in Fig. 5a shows, the kinetic curves exhibited a break-point after the decomposition of 6% of PhOH. During the VUV irradiation, the pH increased from 7.8 to almost 11 (Fig. 5b) probably caused by the reaction of $CO_2^{\bullet-}$ with $^\bullet OH$ which leads to hydroxide ions, and explains the increase in pH. This basic
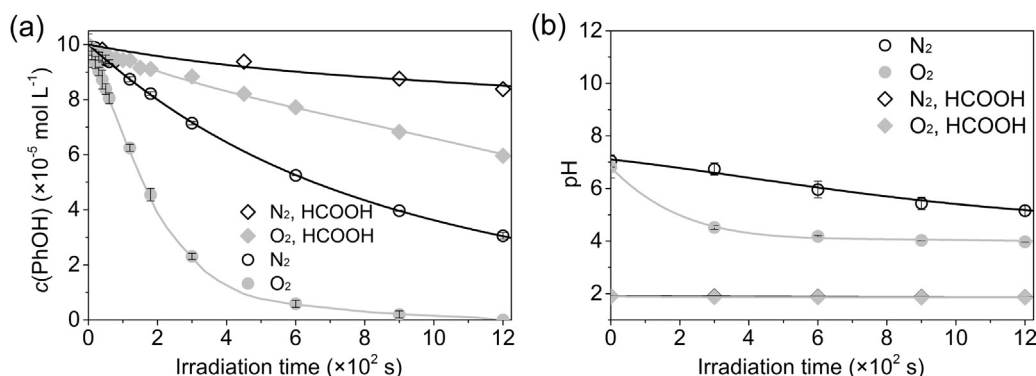

Fig. 4. PhOH concentration (a) and pH (b) versus irradiation time in the absence and in the presence of HCOOH in solutions purged with N_2 or O_2.
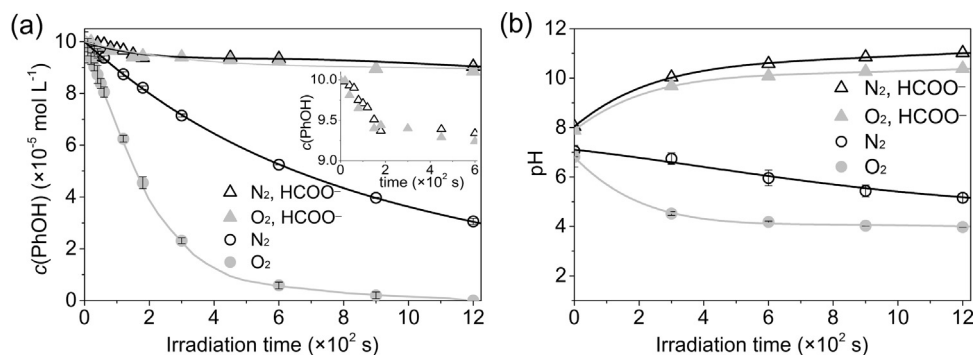
Fig. 5. PhOH concentration (a) and pH (b) versus irradiation time in the absence and in the presence of HCOO⁻ in solutions purged with N_2 or O_2.

condition results that PhOH was present mainly in its deprotonated form (phenolate ion, PhO⁻; $pK_a = 9.88$ [39]) after the breakpoint. This may be the reason of the strong decrease in the rate of transformation of PhOH, since the reactivity of PhO⁻ might be lower than that of PhOH. For the confirmation of this phenomenon, the effect of pH in the range of 7–11 on the initial rate of transformation of PhOH was also investigated in O_2-saturated solutions. The results showed that the rate of transformation of PhOH decreases with the increase of pH (Fig. 6), but this effect is much more significant above pH 10, where PhOH is present mainly in its deprotonated form.

Dissolved O_2 enhanced the rate of transformation of PhOH in each system in which the organic additives were present. In each case, merely the less reactive radicals, such as only $HO_2^\bullet$ (in the case of HCOOH addition), or mainly $O_2^{\bullet-}$ (in the case of HCOO⁻ or t-BuOH addition), were present in these solutions, which suggests that these reactive species in elevated concentration can partly contribute to the transformation of PhOH. It should be noted that, for the different additives, the highest initial rate was observed in the presence of HCOOH, which can be explained by the 5 times higher reaction rate constant of $HO_2^\bullet$ with PhOH than that of $O_2^{\bullet-}$. However, the contribution of these reactive oxygen species to the transformation of PhOH were likely to be negligible, as compared with the contribution of $^\bullet$OH, which is the most relevant reactant.

On the other hand, in each case the concentration of H_2O_2 was found to be much higher in the presence of organic substances than in pure H_2O saturated with O_2 (Fig. 2). This suggests that the main reactions of $HO_2^\bullet$ and $O_2^{\bullet-}$ (formed due to the addition of O_2

to $H^\bullet$ and to elimination from organic peroxyl radicals) are those that result in H_2O_2 formation instead of transformation of PhOH.

4. Conclusions

- A radical scavenger (t-BuOH) and two radical transfer materials (HCOOH and HCOO⁻) were applied in large excess to investigate their effects on the rate of transformation of PhOH and the formation of H_2O_2 in VUV-irradiated, O_2-free and O_2-saturated aqueous solutions.

- The rate of degradation of PhOH increased significantly (up to 3-fold) in the presence of dissolved O_2, most probably because it hindered the recombination of the primary radicals through its reaction with $H^\bullet$, consequently greatly increasing the concentration of $^\bullet$OH. At the same time, the concentrations of $HO_2^\bullet$ and $O_2^{\bullet-}$ also increased, as indicated by the high concentration of H_2O_2 formed, but their contributions to the transformation of PhOH were likely to be negligible.

   In O_2-free solutions, each organic additive reduced the concentrations of both primary radicals and hence the initial rate of PhOH transformation. The effects of HCOOH and HCOO⁻ were more pronounced than that of t-BuOH, which can be explained by the differences in reactivity of the carbon-centred radicals formed, $^\bullet$COOH, $CO_2^{\bullet-}$ and t-$^\bullet$BuOH, respectively.

- In solutions saturated with O_2, there was no significant difference between the initial rates of transformation of PhOH determined in the presence of t-BuOH, HCOOH or HCOONa. From the presented results it seems that HCOOH and HCOONa can be considered as radical scavenger materials as well. In these cases, the contributions of the primary radical-initiated reactions to the transformation of PhOH were negligible, since the most significant species of the radical set were the less reactive $HO_2^\bullet$ or $O_2^{\bullet-}$ (depending on the pH), which even in elevated concentration made merely minor contributions to the transformation of PhOH. The slightly higher initial rate of transformation in the presence of HCOOH can be explained by the 5 times higher reaction rate constant of $HO_2^\bullet$ with PhOH than that of $O_2^{\bullet-}$. At the same time, the relatively high concentrations of the H_2O_2 in the solutions containing organic substances proved that main reactions of $HO_2^\bullet$ and $O_2^{\bullet-}$ results in the formation of H_2O_2 instead of the reaction with PhOH.

- The kinetic data reported can be explained by the variation of the concentration of $^\bullet$OH due to the addition of radical transfer or scavenger materials and the trapping of carbon-centred radicals by O_2. This means that in all 8 cases mentioned in Table 1, $^\bullet$OH is the only relevant reactant for the transformation of PhOH.
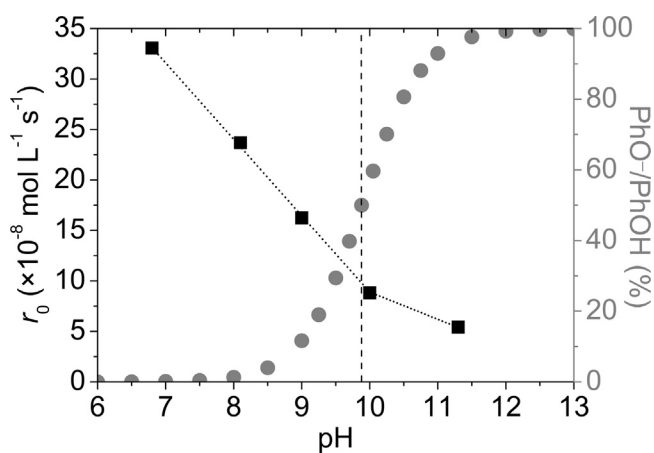

Fig. 6. Effect of pH on the initial rate of transformation of PhOH in solutions purged with O_2 and the ratio PhO⁻/PhOH. The dashed line shows the pK_a of PhOH.

Acknowledgements

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