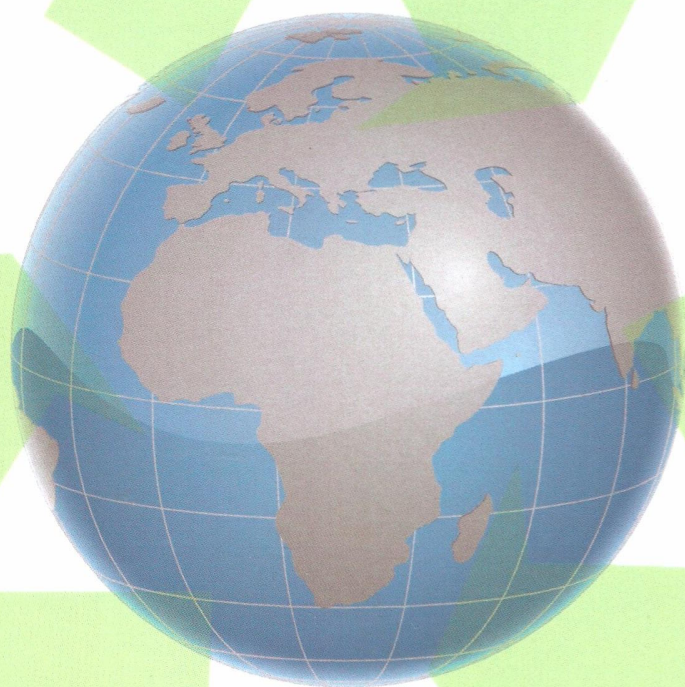


PROCEEDINGS OF  
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ON ANALYTICAL AND ENVIRONMENTAL  
PROBLEMS, WITH SPECIAL EMPHASIS  
ON HEAVY METAL IONS AS CONTAMINANTS

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# THE EFFECT OF THE REACTION CONDITIONS ON THE VACUUM ULTRAVIOLET PHOTOLYSIS OF PHENOL

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## ABSTRACT

Even more attention is focused on Advanced Oxidation Processes (AOPs) from an environmental aspect because of the effective degradation of different organic contaminants, without the addition of chemicals. Using this method, the mineralization of the target compounds takes place in reactions by reactive free radicals. For the optimization of the degradation processes proper knowledge of the mechanisms is needed. Our research therefore tended to affect the radical set by changing the reaction conditions and to notice its effect on the vacuum-ultraviolet photolysis of phenol, which is a simple structured model compound. During the investigations the phenol degradation rate ( $r$ ) and the formation and degradation of aromatic intermediates were checked.

In our experiments aqueous phenol solutions ( $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>) were irradiated by a Xe<sub>2</sub> excimer lamp ( $\lambda_{\text{max}} = 172$  nm) in the presence of different dissolved gases (N<sub>2</sub> or O<sub>2</sub>), and by addition of either *tert*-butanol (*t*-BuOH, in 0.50 mol dm<sup>-3</sup> concentration) as hydroxyl radical ( $\cdot\text{OH}$ ) scavenger or formic acid (HCOOH, 0.05 mol dm<sup>-3</sup> concentration) as  $\cdot\text{OH}$  transfer additives.

In solutions degassed by N<sub>2</sub> bubbling,  $\cdot\text{OH}$  and hydrogen atoms (H $\cdot$ ) generated from water could be responsible for the degradation of phenol. It was concluded that the  $r$  was the highest using O<sub>2</sub>. Dissolved oxygen reacted with H $\cdot$  hindering the recombination reaction between H $\cdot$  and  $\cdot\text{OH}$  and as a consequence increasing the concentration of  $\cdot\text{OH}$  which might contribute to the higher  $r$ .

In the presence of additives the  $r$  decreased. *t*-BuOH applied in a great excess decreased the concentration of reactive  $\cdot\text{OH}$  thus the  $r$  too. In O<sub>2</sub> free solutions formic acid behaved as radical scavenger: it decreased the  $r$  similarly like the *t*-BuOH. Using O<sub>2</sub> and HCOOH moderate  $r$  was measured, which could be caused by the increased concentration of the formed hydroperoxyl radicals/superoxide radical anions (HO<sub>2</sub> $\cdot$ /O<sub>2</sub> $\cdot^-$ ), which might contribute to the degradation of phenol in this higher concentration.

The formed 1,2- and 1,4-dihydroxybenzenes (DHBs) were present in same concentration both in O<sub>2</sub> free and O<sub>2</sub> saturated solutions containing no additives, but using radical transfers DHBs were found in significantly lower concentration.

## INTRODUCTION

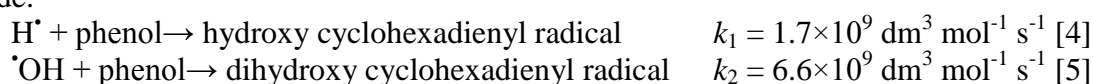
In the last some decades the number of the daily used chemicals increased. Due to the low efficiency of the traditional water treatment techniques in the elimination of toxic compounds: different medicine agents and pesticides might reach the environment and might accumulate in living organisms. It's a serious environmental problem and therefore we should try to minimize their harmful effects. To improve the water purifying techniques the traditional

methods could be completed with the more effective and economic Advanced Oxidation Processes (AOPs). During these processes the first step is usually a reaction of a reactive radical with the organic contaminant, inducing its degradation. Hydroxyl radicals ( $\cdot\text{OH}$ ) are the most reactive and less selective radicals, which react very rapidly (the rate constant being  $10^8$ - $10^{10}$   $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ) with organic and inorganic compounds [1].  $\cdot\text{OH}$  can be generated by different methods, one of them is the vacuum-ultraviolet (VUV) photolysis. During this process excimer lamps emit photons of wavelength shorter than 200 nm to cause the homolytic dissociation of water molecules [1]:



During VUV photolysis  $\cdot\text{OH}$  and hydrogen radicals ( $\text{H}^\cdot$ ) are generated as primary radicals. These are presumably formed in a solvent cage thus their recombination is very favourable [3]. When the system also contains additives, the additive compound and the model molecule compete for the primary radicals. Therefore, less radical may react with the examined compound thus the degradation rate ( $r$ ) of the target molecule is reduced too. Because the reaction between the additives and the primary radicals result in radicals too, these molecules are radical transfers. If the reactivity of the resulted radicals towards organic contaminants is negligible, the radical transfer behaves as a radical scavenger.

In this work phenol was chosen as a model compound to investigate the effect of different reaction conditions on the efficiency of its VUV photolysis. Both of the primary photoproducts of water react with phenol with a reaction rate constant of the same order of magnitude:



However the further transformation of the hydroxy cyclohexadienyl radical yields the phenol molecule and therefore the reaction between the target compound and  $\text{H}^\cdot$  doesn't lead to the degradation of the first [6]. During the degradation of phenol a lot of different aromatic intermediates are formed, like 1,2- and 1,4-dihydroxybenzene (DHB). The generation of these intermediates is primarily initiated by the electrophilic addition of  $\cdot\text{OH}$  on phenol. Because of the directing effect of the OH substituent the ortho (48%) and para (36%)  $\cdot\text{OH}$  addition are favourable, while the meta (8%) and the ipso-addition (8%) has less significance [7]. The formed dihydroxy cyclohexadienyl radical usually reacts with  $\text{O}_2$  molecule, which results in DHB after the elimination of a hydroperoxyl radical ( $\text{HO}_2^\cdot$ ) [6].

## MATERIALS and METHODS

### Materials, experimental setup and reaction conditions

During our experiments 250  $\text{cm}^3$  aqueous phenol (VWR, 100,0%) solutions ( $c_0 = 1.0 \times 10^{-4}$   $\text{mol dm}^{-3}$ ) were irradiated with VUV light produced by a  $\text{Xe}_2$  excimer lamp (Radium Xeradex<sup>TM</sup>, 20 W electrical input power, emitting at  $172 \pm 14$  nm), using different reaction conditions. The solutions were circulated between the thermostated ( $25 \pm 0.5$  °C) reactor and reservoir by a Heidolph peristaltic pump with a flow rate of 375  $\text{cm}^3 \text{min}^{-1}$ . In each case  $\text{N}_2$  (purity 4.5) or pure (4.5)  $\text{O}_2$  ( $c_{\text{O}_2} = 13 \times 10^{-4}$   $\text{mol dm}^{-3}$ ) was introduced with a flow rate of 600  $\text{cm}^3 \text{min}^{-1}$  into the solutions before the reaction and throughout the irradiation. The samples could contain 0.50  $\text{mol dm}^{-3}$  *tert*-butanol (*t*-BuOH, VWR, 100,0%) or 0.05  $\text{mol dm}^{-3}$  formic acid (HCOOH, VWR, 99,0%). Kinetic investigations were started by switching on the lamp. Two or three consecutive measurements were performed in the case of each reaction condition.

## High performance liquid chromatography (HPLC)

The degradation of phenol as well as the qualitative and quantitative determination of the formed aromatic intermediates was followed by HPLC analysis with UV detection using an Agilent 1100 Series equipment and a reversed phase LiChroCART® 150-4.6, RP-18 column with 5 µm particle size. The mobile phase consisted of 35% methanol (VWR, 99,80%) and 65% ultra pure MILLI-Q water (MILLIPORE Milli-Q Direct 8/16). During the separation 20 µl sample was analyzed using an eluent flow rate of 0.800 ml min<sup>-1</sup> at 25 °C and detection wavelength of 210 nm.

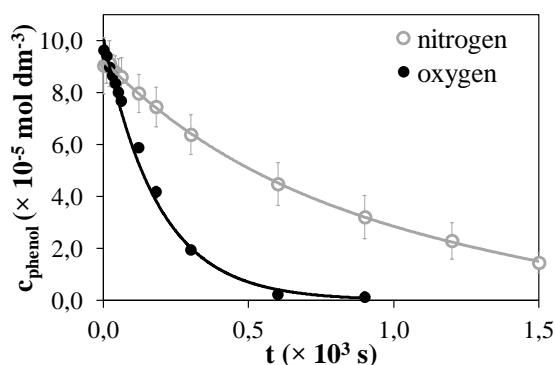
## RESULTS

### Effect of dissolved molecular oxygen

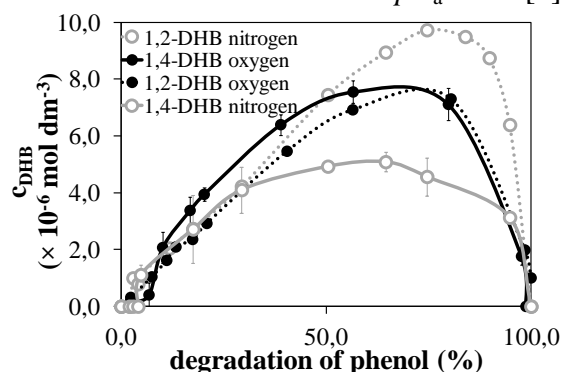
Dissolved molecular O<sub>2</sub> reacts with H<sup>•</sup> and transfers it to HO<sub>2</sub><sup>•</sup>, which has lower reactivity towards organic molecules than <sup>•</sup>OH [1].



The conjugate base pair of this species is the superoxide radical anion [1]:



**Fig. 1** Degradation of phenol in the presence and in the absence of O<sub>2</sub>.

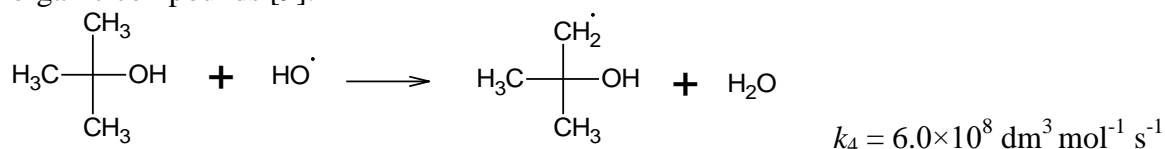


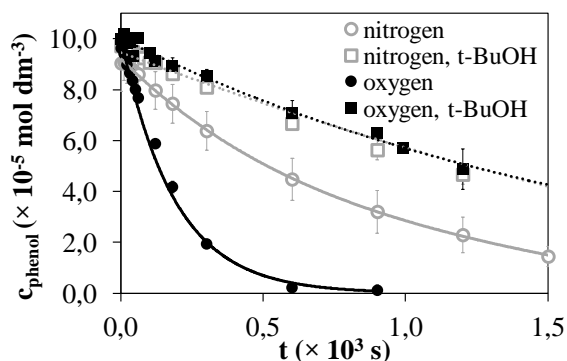
**Fig. 2** Formation and degradation of the DHBs in the presence and in the absence of O<sub>2</sub>.

In O<sub>2</sub> free solutions the recombination of the primary radicals is very favourable therefore phenol competes with H<sup>•</sup> for <sup>•</sup>OH. In O<sub>2</sub> saturated solutions the *r* was significantly higher than in its absence (Fig. 1). Because of the higher value of *k*<sub>3</sub> compared to *k*<sub>1</sub> and that the concentration of dissolved O<sub>2</sub> (c<sub>O<sub>2</sub></sub> = 13 × 10<sup>-4</sup> mol dm<sup>-3</sup>) was with one order of magnitude higher than the initial concentration of phenol (c<sub>0</sub> = 1.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>), presumably H<sup>•</sup> reacts particularly with O<sub>2</sub>. Accordingly, the effect of dissolved molecular O<sub>2</sub> could reveal in the decrease of the concentration of H<sup>•</sup> and the increase of the concentration of <sup>•</sup>OH and HO<sub>2</sub><sup>•</sup>/O<sub>2</sub><sup>•-</sup>. Interestingly, DHBs formed in a valuable concentration in O<sub>2</sub> free samples too (Fig. 2). The ratio of the concentrations of 1,2- and 1,4-DHBs (48:36) was similar given in the literature in O<sub>2</sub> saturated solutions [7].

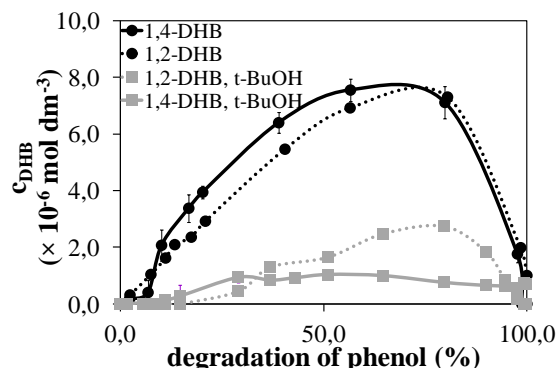
### Effect of *tert*-butanol

*Tert*-butanol is a well known <sup>•</sup>OH scavenger because it reacts with <sup>•</sup>OH with large rate constant and the formed 2,2-dimethyl-2-hydroxyethyl radical (*t*-BuOH) does not react with the organic compounds [9].





**Fig. 3** The effect of *t*-BuOH on the phenol degradation in the presence and in the absence of O<sub>2</sub>.



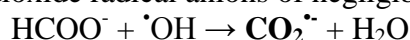
**Fig. 4** The effect of *t*-BuOH on the concentration of DHBs in the presence of O<sub>2</sub>.

The presence of *t*-BuOH ( $c_0 = 0.50 \text{ mol dm}^{-3}$ ) decreased the  $r$  significantly to the same rate both in O<sub>2</sub> free and in O<sub>2</sub> saturated solutions of phenol ( $c_0 = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) (Fig. 3). Its explanation might be in the used large excess of *t*-BuOH (5000×), which could decrease the concentration of the primary radicals to same value in these conditions.

This radical scavenger also decreased significantly the concentration of the formed DHBs in O<sub>2</sub> free and in O<sub>2</sub> saturated solutions as well (Fig. 4), most probably because the decrease of the  $\cdot\text{OH}$  concentration also reduced the plausibility of DHB formation.

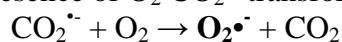
#### Effect of formic acid

Formic acid is a generally used radical transfer, too. Formate ions convert reactive  $\cdot\text{OH}$  to carbon dioxide radical anions of negligible reactivity [9]:

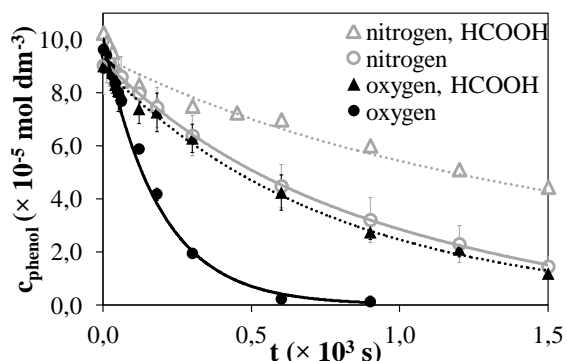


$$k_5 = 3.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} [4]$$

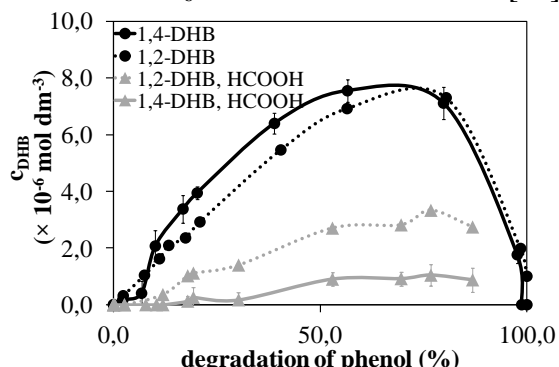
In the presence of O<sub>2</sub> CO<sub>2</sub><sup>•-</sup> transform to HO<sub>2</sub><sup>•</sup>/O<sub>2</sub><sup>•-</sup>:



$$k_6 = 4.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} [10]$$



**Fig. 5** The effect of formic acid on the degradation of phenol in the presence and in the absence of O<sub>2</sub>.



**Fig. 6** The effect of formic acid on the concentration of DHBs in the presence of O<sub>2</sub>.

In O<sub>2</sub> free conditions the large excess (500×) of HCOOH ( $c_0 = 0.05 \text{ mol dm}^{-3}$ ) reduced the phenol ( $c_0 = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ) degradation to the same rate as the *t*-BuOH (Fig. 3, 5), thus it operated as a  $\cdot\text{OH}$  scavenger as well. In O<sub>2</sub> saturated solutions both primary radicals are transformed to HO<sub>2</sub><sup>•</sup>/O<sub>2</sub><sup>•-</sup>. The higher value of  $r$  compared to the O<sub>2</sub> free conditions suggests that HO<sub>2</sub><sup>•</sup>/O<sub>2</sub><sup>•-</sup> might contribute to the degradation of phenol in this higher concentration.

The diminished concentration of  $\cdot\text{OH}$  decreased the concentration of DHBs (Fig. 6). The ratio of the concentrations of 1,2- and 1,4-DHBs differs from that of the literature, which suggests the formation of DHBs also through phenoxy radicals [7, 11].

## CONCLUSIONS

- During our research different reaction conditions were applied to investigate the effect of the radical set on the VUV photolysis of phenol and on the formation and degradation of the aromatic intermediates.
- The  $r$  increased significantly in the presence of dissolved molecular  $O_2$  because it hindered the recombination of the primary radicals and increased the concentration of  $\cdot OH$  and  $HO_2\cdot/O_2\cdot^-$ .
- The great excess of  $t$ -BuOH reduced the concentration of primary radicals to the same value in  $O_2$  free and  $O_2$  saturated solutions as well, thus it decreased the  $r$  too.
- In  $O_2$  free conditions the HCOOH behaved as radical scavenger too, it decreased the  $r$  by transforming the  $\cdot OH$  to  $CO_2\cdot^-$  of negligible reactivity.
- In the presence of  $O_2$  and HCOOH both primary radicals are converted to  $HO_2\cdot/O_2\cdot^-$ , which might contribute to the degradation of phenol in this higher concentration.
- The decreased concentration of 1,2- and 1,4-DHB in the presence of additives indicates the decrease of the concentration of  $\cdot OH$  both in  $O_2$  free and  $O_2$  saturated solutions.

## ACKNOWLEDGMENTS

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