The role of reactive oxygen species in the vacuum ultraviolet photolysis of four nonsteroidal anti-inflammatory drugs

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1. Introduction and objectives

Since the traditional wastewater treatment techniques are based on biological methods, and there are several pollutants which can not be eliminated by the used microorganisms, the decontamination of these waters is of utmost interest nowadays. Nonsteroidal anti-inflammatory drugs (NSAIDs) are usually reported to be recalcitrant water contaminants and therefore ibuprofen (IBU), ketoprofen (KETO), naproxen (NAP) and diclofenac (DICL) were chosen as target molecules and phenol (PhOH) as a model compound.

The application of advanced oxidation processes (AOPs) may solve the above mentioned problem. AOPs are based on the generation of reactive radicals, which can induce the transformation of the contaminants. Although there is plenty of information about the reactions of the most reactive radical, the hydroxyl radical (HO\(^\cdot\)), only a few data is given concerning the less reactive radicals, which might also contribute to the degradation of the pollutant molecules if their concentration is increased.

Vacuum ultraviolet (VUV) photolysis is a suitable method among the AOPs to study the direct reactions and the effects of different parameters (e.g. the presence of dissolved O\(_2\) or radical transfer molecules) on the radical set and on the degradation of organic contaminants, since the generated radical set is known, using this technique.

Hydroperoxyl radicals/superoxide radical ions (HO\(_2\)\(^{-}\)/O\(_2\)\(^{-}\)) are the most important oxygen containing species along HO\(^\cdot\). The concentration of H\(_2\)O\(_2\) (c\(_{H_2O_2}\)) refers to their concentration (c\(_{HO_2^{-}/O_2^{-}}\)) and therefore, the c\(_{H_2O_2}\) was planned to be measured during the VUV photolysis of the target molecules.

![Fig. 1. The effect of different radical transfers on the radical set generated during the VUV photolysis of water.](image)

As it can be seen from Fig. 1, dissolved O\(_2\) affects the radical set from several routes. Therefore, the aim of this study was to investigate the effect of the presence of O\(_2\) on the initial transformation of the pollutants, on the formation and transformation of their main
aromatic by-products and on their mineralization. To study the relatively increasing effect of dissolved O₂, experiments were planned in solutions containing the contaminant molecules in two different initial concentrations.

In the presence of both dissolved O₂ and formate ions, all of primary reactive species of VUV photolysis (HO• and hydrogen atoms/hydrated electrons (H•/e_{aq}−)) transform to HO₂•/O₂•− (Fig. 1). Additionally, altering the pH of the solution the ratio of HO₂• and O₂•− might also be influenced. Thus, the experiments aimed also the investigation of the effects of HO₂• and O₂•− on the initial transformation rates of the target compounds.

In the presence of both dissolved O₂ and radical scavengers (methanol or tert-butanol), peroxyl radicals (•OOCH₂OH or •OOCH₂C(CH₃)₂OH) are present in the solution along with HO₂•/O₂•− (Fig. 1). The aim of this study was to make comparison between the initial transformation of the pollutant molecules in the presence of formate ions and in the presence of radical scavengers, to compare the reactivity of these reactive oxygen species (ROS) with each other.

The radical set is affected also by the contaminants themselves, and therefore the VUV photolysis of the target molecules was planned in four different initial concentrations (c₀).

Since no information was found in the literature concerning the VUV degradation of IBU, KETO, NAP or DICL, the aim of this work was also to give suggestions for the chemical structures of the formed aromatic by-products and to give a tentative mechanism of their formation.

The realization of the aims above could contribute to improve the efficiency of AOPs.
Methods

Two types of experimental setups were used for the VUV investigations. The treated solution was circulated between a thermostated reactor and a reservoir in both cases. The 250 cm$^3$ or 2 dm$^3$ solution was irradiated with either a 20 W or with a 100 W xenon excimer lamp, respectively, emitting at 172±14 nm. N$_2$, O$_2$ or air was injected in the irradiated solution to achieve deoxygenated, O$_2$- or air-saturated conditions, respectively.

Samples containing the pollutant molecules were analyzed on an Agilent 1100 series LCMSD VL system. For determination of the total organic carbon content of the solutions, a multi N/C 3100 instrument (Analytik Jena AG) was used.

The apparent reaction rate constants ($k'$) of the degradation of the investigated compounds were determined by performing a nonlinear model fit on the concentrations measured during the HPLC analyses, with the help of Mathematica 8 (Wolfram) software. It should be mentioned that our system is very inhomogeneous. The VUV photons are absorbed in a very thin water layer (< 0.1 mm) and therefore only a thin-walled hollow cylindrical volume of solution is irradiated, near the quartz/water interface. Further, the experimental setup consisted of a partly-irradiated reactor and a reservoir, the determined (apparent) $k'$ values therefore referring to the overall transformation rate of the target molecules under the experimental conditions applied.
Novel scientific results

**T1. During the initial VUV transformation of the studied contaminants the concentration of HO$_2^\cdot$/O$_2^-$ increases.**

The VUV photolysis of oxygenated PhOH, IBU and KETO solutions showed that during the initial transformation of the contaminant molecules the $c_{H_2O_2}$ increases, which could be a proof for the increase of the $c_{HO_2^\cdot/O_2^-}$. Although the reactivity of HO$_2^\cdot$/O$_2^-$ is usually reported to be lower than that of H$^\cdot$ [1], in an elevated concentration they may also contribute to the degradation of organic contaminants [2].

**T2. The role of reductive (H$^\cdot$/e$_{aq}^-$) and oxidative (HO$_2^\cdot$/O$_2^-$ and HO$^\cdot$) reactive species in the transformation of organic pollutants depends strongly on the structure of the contaminant molecules, which influences their reaction rate constants with the mentioned radicals.**

The initial VUV transformation rates ($r_0$) of PhOH were higher in the presence of dissolved O$_2$, although they were lower in the case of irradiating NAP and $1.0 \times 10^{-5}$ mol dm$^{-3}$ IBU solutions. In the case of KETO, DICL and $1.0 \times 10^{-4}$ mol dm$^{-3}$ IBU solutions the $r_0$ values didn’t depend on the $c_{O_2}$ (Table I).

<table>
<thead>
<tr>
<th>comp.</th>
<th>gas</th>
<th>$c_0 = 1.0 \times 10^{-5}$ mol dm$^{-3}$</th>
<th>$c_0 = 1.0 \times 10^{-4}$ mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$r_0$ ($\times 10^{-7}$ mol dm$^{-3}$ s$^{-1}$)</td>
<td>SD ($\times 10^{-7}$ mol dm$^{-3}$ s$^{-1}$)</td>
</tr>
<tr>
<td>PhOH</td>
<td>O$_2$</td>
<td>2.4</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>N$_2$</td>
<td>1.9</td>
<td>0.05</td>
</tr>
<tr>
<td>IBU</td>
<td>O$_2$</td>
<td>1.2</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>N$_2$</td>
<td>1.6</td>
<td>0.06</td>
</tr>
<tr>
<td>KETO</td>
<td>O$_2$</td>
<td>2.8</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>N$_2$</td>
<td>2.7</td>
<td>0.04</td>
</tr>
<tr>
<td>NAP</td>
<td>O$_2$</td>
<td>1.4</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>N$_2$</td>
<td>3.2</td>
<td>0.20</td>
</tr>
<tr>
<td>DICL</td>
<td>O$_2$</td>
<td>1.9</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>N$_2$</td>
<td>1.8</td>
<td>0.08</td>
</tr>
</tbody>
</table>
In the case of PhOH, dissolved O₂ could prevent the recombination of H*/e⁻ and HO•, it converts reductive H*/e⁻ to oxidative HO₂*/O₂•−, and at the same time it may hinder the backward reactions of R• and (RHOH)* (generated in the reactions of the pollutant molecules and HO•). These effects could result in the increase of the initial transformation rate of PhOH in the presence of O₂.

In contrast, the results of the VUV photolysis of NAP and 1.0 × 10⁻⁵ mol dm⁻³ IBU solutions suggested that in this case the contribution of H*/e⁻ to the transformation of the target molecules was much more significant than that of HO₂*/O₂•− [3]. In the case of KETO, DICL and 1.0 × 10⁻⁴ mol dm⁻³ IBU solutions, where the r₀ values didn’t depend on the cO₂, showed, that although the concentration of H*/e⁻ is decreased in the presence of O₂, this effect may be compensated by the increased concentration of ROS [4].

**T3. The presence of dissolved O₂ was found to be essential during the effective VUV induced decontamination of NSAID-containing solutions.**

Since in the absence of dissolved O₂ the rate of mineralization was so low, it seems that in deoxygenated solutions some undetected recalcitrant by-products (maybe the dimers and oligomers of the target molecules) were formed [4].

**T4. The reaction rate of HO₂*/O₂•− with organic compounds depends highly on the structure of the target molecules.**

Table II. The initial VUV transformation rates of the investigated compounds in case of converting the majority of the radicals to HO₂*/ or to O₂•−.

<table>
<thead>
<tr>
<th>comp.</th>
<th>HO₂•− r₀ (× 10⁻⁸ mol dm⁻³ s⁻¹)</th>
<th>SD (× 10⁻⁸ mol dm⁻³ s⁻¹)</th>
<th>O₂•− r₀ (× 10⁻⁸ mol dm⁻³ s⁻¹)</th>
<th>SD (× 10⁻⁸ mol dm⁻³ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhOH</td>
<td>13.0</td>
<td>1.00</td>
<td>1.1</td>
<td>0.10</td>
</tr>
<tr>
<td>IBU</td>
<td>2.2</td>
<td>0.20</td>
<td>5.2</td>
<td>0.20</td>
</tr>
<tr>
<td>KETO</td>
<td>3.2</td>
<td>0.05</td>
<td>8.8</td>
<td>0.30</td>
</tr>
<tr>
<td>NAP</td>
<td>2.2</td>
<td>0.20</td>
<td>1.1</td>
<td>0.03</td>
</tr>
</tbody>
</table>

If both formate ions and O₂ are present in the solution, almost all primary radicals of VUV photolysis can be converted to HO₂*/O₂•−. Under acidic conditions most of the radicals appear in form of HO₂*, while under basic conditions they are almost completely transformed to O₂•−. The results of the VUV photolysis of the studied compounds under
these conditions suggested that during the transformation of PhOH and NAP, the contribution of HO$_2^\bullet$ [5], while in the case of IBU and KETO, the contribution of O$_2^{-•}$ was higher among HO$_2^\bullet$/O$_2^{-•}$ (Table II).

Because of the low solubility of DICL below pH = 5.8, the contribution of HO$_2^\bullet$ and O$_2^{-•}$ to the transformation of this molecule was studied by performing experiments in the presence and in the absence of phosphates. In solutions prepared in phosphate buffer (PB) HO$_2^\bullet$/O$_2^{-•}$ was present mainly in the form of O$_2^{-•}$ during the whole treatment. In the case of DICL dissolved in Milli-Q water, the majority of O$_2^{-•}$ was converted to HO$_2^\bullet$, using longer irradiation times (t > 180 s). After 180 s of irradiation, the decay of DICL was slightly increased in Milli-Q water. Additionally, the concentrations of the aromatic by-products were higher in the presence of PB. These results suggested that the reaction rates of DICL and its by-products with O$_2^{-•}$ are probably lower than those with HO$_2^\bullet$ [4].

**T5. The contribution of the peroxyl radicals formed from methanol and tert-butanol (\textit{OOCH$_2$OH and \textit{OOCH$_3$C(CH$_3$)$_2$OH, respectively}) to the VUV transformation of the studied contaminants may be higher than that of HO$_2^\bullet$/O$_2^{-•}$.**

Table III. The ratio of the initial VUV transformation rates of the investigated compounds in the presence of different radical transfers.

<table>
<thead>
<tr>
<th>comp.</th>
<th>$r_0$ (O$_2$)/$r_0$ (HO$_2^\bullet$)</th>
<th>$r_0$ (O$_2$)/$r_0$ (O$_2^{-•}$)</th>
<th>$r_0$ (O$<em>2$)/$r_0$ (lower $c</em>{rad.scav}$)</th>
<th>$r_0$ (O$<em>2$)/$r_0$ (higher $c</em>{rad.scav}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhOH</td>
<td>3.4</td>
<td>40.0</td>
<td>5.3</td>
<td>8.0</td>
</tr>
<tr>
<td>IBU</td>
<td>24.1</td>
<td>10.2</td>
<td>1.8</td>
<td>n.m. *</td>
</tr>
<tr>
<td>KETO</td>
<td>31.3</td>
<td>11.4</td>
<td>1.1</td>
<td>1.9</td>
</tr>
<tr>
<td>NAP</td>
<td>30.9</td>
<td>60.2</td>
<td>3.3</td>
<td>5.0</td>
</tr>
<tr>
<td>DICL</td>
<td>n.m.</td>
<td>n.m.</td>
<td>1.5</td>
<td>2.6</td>
</tr>
</tbody>
</table>

The ratios of the initial VUV transformation rates of the studied molecules in the presence of dissolved O$_2$ and in the presence of both O$_2$ and formate ions (to convert the radicals to HO$_2^\bullet$/O$_2^{-•}$) ($r_0$ (O$_2$)/$r_0$ (HO$_2^\bullet$) or $r_0$ (O$_2$)/$r_0$ (O$_2^{-•}$)) with the ratios of the transformation rates in the presence of dissolved O$_2$ and in the presence of both O$_2$ and radical scavengers (CH$_3$OH or tert-butanol) ($r_0$ (O$_2$)/$r_0$ (lower $c_{rad.scav}$) or $r_0$ (O$_2$)/$r_0$ (higher $c_{rad. scav}$)) were compared. From Table X it can be seen that the former values are significantly (in almost all cases with one order of magnitude) higher than the latter ones.
The only exception is the case of irradiating PhOH in the presence of both O₂ and formate ions at acidic pH.

The reason of the former surprising observation might be that the contribution of the peroxyl radicals (formed in the presence of both O₂ and the radical scavengers: \( \cdot \text{OOCH}_2\text{OH} \) and \( \cdot \text{OOCH}_2\text{C(CH}_3)_2\text{OH} \), respectively) to the transformation of the contaminants may be higher than that of \( \text{HO}_2^-/\text{O}_2^- \) (formed in the presence of both O₂ and formate ions). The contribution of these peroxyl radicals to the degradation of organic pollutants should therefore not be neglected. Thus, methanol and tert-butanol should also be considered as radical transfers instead of radical scavengers.

The relatively low value of \( r_0 (\text{O}_2)/r_0 (\text{HO}_2^-) \) in case of irradiating PhOH suggests that the reaction rate constants of \( \text{HO}_2^- \) are lower in case of the NSAIDs than that of PhOH (\( 2.7 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) [5]). Therefore, the contribution of \( \text{HO}_2^- \) to the degradation of the contaminants seems to be negligible in case of the studied drugs and it seems to have a minor significance in case of PhOH.

**T6.** In oxygenated solutions, the steady-state concentration of \( \text{HO}^* \) ([\( \text{HO}^* \]SS) decreases with the increase of \( c_0 \), which results in the decrease of the apparent first-order VUV degradation rate constants (\( k' = k \times [\text{HO}^*]_{\text{SS}} \)).

If the \( c_0 \) is fixed, the pseudo-first-order approach is suitable for a description of the degradation kinetics of the VUV photolysis of the investigated contaminants. However, in oxygenated solutions, the apparent first-order rate constants (\( k' = k \times [\text{HO}^*]_{\text{SS}} \)) decreased in almost all cases with the increase of the \( c_0 \). The reason of these observations might be that at higher \( c_0 \), more \( \text{HO}^* \) are involved in reactions with the NSAIDs and the steady-state concentration of \( \text{HO}^* \) ([\( \text{HO}^* \]SS) therefore decreases, along the constant value of \( k \) [3, 4]. In case of PhOH, the results correlate well with the work of Sato et al. [6].

**T7.** H-abstraction, \( \text{HO}^*/\text{H}^* \)-addition and decarboxylation reactions, as well as the reactions of the peroxyl radicals (formed from the target molecules) are the key steps during the VUV degradation of the studied NSAIDs. Some of these reactions take place only in oxygenated solutions, while others both in the presence and absence of dissolved O₂.

During the VUV photolysis of the investigated NSAIDs four aromatic by-products of IBU and KETO and three by-products of NAP and DICL were detected. With the help of
the HPLC-MS analysis, suggestions could be given for the chemical structures of these compounds. At the same time, a tentatively determined mechanism of the VUV photolysis of the studied drugs could be given (Figs. 2–5). The formation of the by-products of KETO and NAP could be interpreted with the reactions of the aliphatic chains, the formation of the by-products of DICL with the reactions of the aromatic rings [4], while the formation of the by-products of IBU with the reactions of both the aromatic ring and the aliphatic chains.

Fig. 2. Possible pathway of formation of four VUV degradation by-products of IBU.
Fig. 3. Possible pathway of formation of four VUV degradation by-products of KETO.
Fig. 4. Possible pathway of formation of three VUV degradation by-products of NAP.
Fig. 5. Possible pathway of formation of three VUV degradation by-products of DICL.
References


Scientific activity

Papers

Papers related to the PhD Thesis

   IF: 1.23; independent citation: 1

   IF: 3.925; independent citations: 2

   IF: 3.258; independent citation: –

Papers not directly related to the PhD Thesis

   IF: 0.599; independent citation: 1

   IF: 1.004; independent citations: 5


IF: 2.656; independent citations: 4


IF: 0.806; independent citation: –


IF: 1.189; independent citation: –

Cumulative impact factor: 14.667
Total number of independent citations: 10

Book chapters
Book chapters related to the PhD Thesis


Conference participations

PhD Thesis related participations


*Conference participations not related to the PhD Thesis*


