Hydroxyl Radical Induced Oxidation of Theophylline in Water: A Kinetic and Mechanistic Study

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(Electronic Supplementary Information)
Table S1 - The spectral and kinetic parameters of the reaction of $^\cdot$OH, $\text{SO}_4^{\cdot-}$, $\text{N}_3^{\cdot}$ and $\text{O}^{\cdot-}$ with theophylline

<table>
<thead>
<tr>
<th>Radical</th>
<th>pH</th>
<th>$\lambda_{\text{max}}$ / nm</th>
<th>$k_2$ / $10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^\cdot$OH</td>
<td>5.9</td>
<td>330, 500</td>
<td>8.22 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>10.2</td>
<td>340</td>
<td>7.11 ± 0.07</td>
</tr>
<tr>
<td>$\text{SO}_4^{\cdot-}$</td>
<td>6</td>
<td>350</td>
<td>7.51 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>9.3</td>
<td>350</td>
<td>5.37 ± 0.03</td>
</tr>
<tr>
<td>$\text{N}_3^{\cdot}$</td>
<td>4</td>
<td>350</td>
<td>4.05 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>6.1</td>
<td>340</td>
<td>7.61 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>9.6</td>
<td>350</td>
<td>8.42 ± 0.06</td>
</tr>
<tr>
<td>$\text{O}^{\cdot-}$</td>
<td>~ 13</td>
<td>320, 350</td>
<td>1.95 ± 0.02</td>
</tr>
</tbody>
</table>
Figure S1 – MS/MS spectrum of 1-methylxanthine (ii)
Figure S2 - MS/MS spectrum of 3-methylxanthine (iii)
Figure S3 - MS/MS spectrum of 1,3-dimethyluric acid (i)
**Figure S4** - Mass spectrum of 1,3-dimethyluric acid (i) in positive ionization mode
Figure S5 - Mass spectrum of 1-methylxanthine (ii) in negative ionization mode
Figure S6 - Mass spectrum of 3-methylxanthine (iii) in positive ionization mode
Figure S7 - MS/MS spectrum of 1-dimethyluric acid (iv) and 3-dimethyluric acid (v) in positive ionization mode.
Figure S8 - Mass spectrum of xanthine (vi) in positive ionization mode
Figure S9 - Mass spectrum of 1/3-methyl tetrahydro-1H-purine-2,6-dione (vii) in negative ionization mode
Figure S10 - Mass spectrum of 8-hydroxy-1/3-methyl-3,7,8,9-tetrahydro-1H-purine-2,6-dione (viii) in positive ionization mode
Figure S11 - Mass spectrum of 5/6-amino derivative of 5/6-hydroxy-1,3-dimethylpyrimidine-2,4(1H,3H)-dione (ix) in positive ionization mode
Figure S12 - Mass spectrum of 5/6-amino derivative of 1/3- methylpyrimidine-2,4(1H,3H)-dione (x) in positive ionization mode
Figure S13 - Mass spectrum of 5/6-aminopyrimidine-2,4(1H,3H)-dione (xi) and 5/6-amino derivative of 5/6-hydroxydihydropyrimidine-2,4(1H,3H)-dione (xii) in positive ionization mode
Figure S14 - Mass spectrum of 5/6-aminopyrimidine-2,4(1H,3H)-dione (xi) in negative ionization mode
Figure S15 - Mass spectrum of 1/3-methylpyrimidine-2,4(1H,3H)-dione (xiii) in positive ionization mode
Figure S16 - Mass spectrum of 5,6-diaminopyrimidine-2,4(1H,3H)-dione (xiv) in positive ionization mode
Figure S17 - Decay traces at 320 nm (Red) and 350 nm (Black) in the case of reaction of O$^\cdot$ with theophylline.
Figure S18 - Transient absorption spectrum of theophylline ($1 \times 10^{-4} \text{ mol dm}^{-3}$) recorded during its reaction with SO$_4^{\bullet-}$ after (●) 347 μs (pH 6.0) and with N$_3^{\bullet}$ after (○) 328 μs (pH 6.1).
Figure S19 - UV-Vis Spectrum of theophylline at pH 6 and 10.1.
Figure S20- Plot of absorbance of transient at 330 nm obtained by the reaction of theophylline with $^\bullet$OH against pH.
Figure S21 - Percentage degradation of theophylline in N₂ purged (Red) and aerated (Black) conditions as a function of time.