Electronic Supplementary Material (ESM)

to

On the Photolysis of simple Anions and neutral Molecules as Sources of O-/ OH, SOx- and Cl in Aqueous Solution

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Annex I Thermochemistry of the dissociation processes in aqueous solution

Table S9: Applied bond dissociation energies (BDEs, kJ mol\(^{-1}\))

Annex References
**Table S1:** Summary of available absolute decadic absorption coefficients from the literature for \( \text{SO}_4^{2-} \) in the range of the absorption maximum at \( \lambda = 450 \text{ nm} \).

<table>
<thead>
<tr>
<th>Authors (Year)</th>
<th>( \varepsilon_{10} , / , \text{l mol}^{-1} \text{ cm}^{-1} )</th>
<th>Ref.</th>
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<tr>
<td>Dogliotti and Hayon (1967)</td>
<td>460</td>
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<tr>
<td>Hayon and McGarvey (1967)</td>
<td>450</td>
<td>[2]</td>
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<tr>
<td>Roebke et al. (1969)</td>
<td>1100</td>
<td>[3]</td>
</tr>
<tr>
<td>Chawla and Fessenden (1975)</td>
<td>1600</td>
<td>[4]</td>
</tr>
<tr>
<td>McElroy (1990)</td>
<td>1600 ± 100</td>
<td>[5]</td>
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<td>Buxton et al. (1990)</td>
<td>1500 ± 50</td>
<td>[6]</td>
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**Table S2a:** Mechanisms for the simulation calculation

<table>
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<th>Reaction</th>
<th>( k , / , \text{l mol}^{-1} \text{ s}^{-1} )</th>
<th>Ref. ( k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HSO}_5^- + \text{hv}(\lambda = 248 \text{ nm}) \rightarrow \text{OH} + \text{SO}_4^{2-} ) \hfill (R-28)</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>( \cdot \text{OH} + \text{HSO}_5^- \rightarrow \text{H}_2\text{O} + \text{SO}_4^{2-} ) \hfill (R-29)</td>
<td>( 1.7 \cdot 10^7 )</td>
<td>[7]</td>
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<tr>
<td>( \text{SO}_4^{2-} + \text{HSO}_5^- \rightarrow \text{HSO}_4^- + \text{SO}_4^{2-} ) \hfill (R-30)</td>
<td>( \leq 1 \cdot 10^6 )</td>
<td>[8]</td>
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<tr>
<td>( \text{SO}_4^{2-} + \text{SO}_4^- \rightarrow \text{S}_2\text{O}_8^{2-} + \text{O}_2 ) \hfill (R-31a)</td>
<td>( 1.25 \cdot 10^8 )</td>
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<td>( \text{SO}_4^{2-} + \text{SO}_4^- \rightarrow 2 \text{SO}_4^2^- + \text{O}_2 ) \hfill (R-31b)</td>
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<td>( \text{SO}_4^- + \text{SO}_4^- \rightarrow \text{S}_2\text{O}_8^{2-} ) \hfill (R-22)</td>
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**Table S2b:** Applied initial concentrations and absorption coefficients for the simulation calculation.

<table>
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<th>Species</th>
<th>( c(t=0) , / , \text{ mol l}^{-1} )</th>
<th>( \varepsilon , (280 \text{ nm}) , / , \text{l mol}^{-1} \text{ cm}^{-1} )</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td>( \text{HSO}_5^- )</td>
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<td>( \text{SO}_4^- )</td>
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Table S3: Results to determine the absolute quantum yields of the SO$_4^-$ formation from the photolysis of HSO$_5^-$ at $\lambda = 248$ nm.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$\lambda$ / nm</th>
<th>$A$ (SO$_4^-$)</th>
<th>$t$ / $\mu$s</th>
<th>$10^6$ c$_0$ (SO$_4^-$) mol l$^{-1}$</th>
<th>$10^6$c$_{t=0}$ (SO$_4^-$) mol l$^{-1}$</th>
<th>$10^{-16}$ N (SO$_4^-$)</th>
<th>$W_{\text{LASER}}$ / mJ</th>
<th>$10^{-17}$ N$_{\text{ABS}}$</th>
<th>$\Phi$</th>
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<td>405</td>
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Figure S1: Aqueous phase spectra of SO$_3^-$ and SO$_5^-$ from the photolysis of S$_2$O$_6^{2-}$ at $\lambda = 193$ nm at 298 K.
Table S4: Results to determine the absolute quantum yields of the SO$_3^-$ formation from the photolysis of S$_2$O$_6^{2-}$ at $\lambda = 193$ nm.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$\lambda$ / nm</th>
<th>$\varepsilon_{10}(\text{SO}_x^-)$ l mol$^{-1}$ cm$^{-1}$</th>
<th>$\lambda$(SO$_x^-$)</th>
<th>t / $\mu$s</th>
<th>$10^7$ c$_i$(SO$_x$) mol l$^{-1}$</th>
<th>$10^7$c$_{t=0}$(SO$_x^-$) mol l$^{-1}$</th>
<th>$10^{-16}$ N (SO$_4^-$)</th>
<th>W$_{\text{LASER}}$/ mJ</th>
<th>$10^{-16}$ N$_{\text{ABS}}$</th>
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<td>3.25</td>
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<td>100</td>
<td>2.93</td>
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Table S5: Concentrations of the chlorine-containing compounds present in the carried out experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Abs.*</th>
<th>[Cl₂]/mol 1⁻¹</th>
<th>[HOCl] = [Cl⁻]/mol 1⁻¹</th>
<th>[Cl₃⁻]/mol 1⁻¹</th>
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<tbody>
<tr>
<td>CL2-1</td>
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<td>1.6·10⁻⁹</td>
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<td>CL2-3</td>
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<td>4.7·10⁻⁴</td>
<td>1.9·10⁻⁹</td>
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</table>

*: Measured absorption in the mother solution at \(\lambda=325\) nm
Table S6: Parameter for the evaluation of the quantum yields from the HOCl photolysis in aqueous solution. $\lambda = 248$ nm, $T = 298$ K, $[\text{HOCl}] = 4.4 \times 10^{-4} \text{mol l}^{-1}$

<table>
<thead>
<tr>
<th>$\lambda$ / nm</th>
<th>A (Cl)</th>
<th>$t$ / ns</th>
<th>$10^7 c_t$(Cl) mol l$^{-1}$</th>
<th>$10^6 c_{\text{v=0}}$(Cl) mol l$^{-1}$</th>
<th>$10^{-16}$ N (Cl)</th>
<th>$W_{\text{LASER}}$ / mJ</th>
<th>$10^{-16} N_{\text{ABS}}$</th>
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Table S7: Sink reactions for the chlorine atom in the Cl₂/HOCl-system. [HOCl] = [Cl\(^-\)] = 4.4\(\times\)10\(^{-4}\) mol l\(^{-1}\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(k_{2nd} / \text{l mol}^{-1} \text{s}^{-1})</th>
<th>(k_{1st} / \text{s}^{-1})</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>Cl(^-) + Cl(^-) \rightarrow Cl₂</td>
<td>1.0(\times)10(^8)</td>
<td>---</td>
<td>[11]</td>
</tr>
<tr>
<td>Cl(^-) + HOCl \rightarrow HCl + -OCl</td>
<td>3.0(\times)10(^9)</td>
<td>1.3(\times)10(^6)</td>
<td>[11]</td>
</tr>
<tr>
<td>Cl(^-) + Cl(^-) \rightarrow Cl₂(^-)</td>
<td>2.1(\times)10(^10)</td>
<td>9.2(\times)10(^6)</td>
<td>[11]</td>
</tr>
<tr>
<td>Cl(^-) + H(_2)O \rightarrow H(^+) + Cl(^-) + -OH</td>
<td>---</td>
<td>2.5(\times)10(^5)</td>
<td>[5]</td>
</tr>
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</table>
Table S8: Parameter for the evaluation of the quantum yields from the chloroacetone photolysis in aqueous solution. $\lambda = 248$ nm, $T = 298$ K, $[\text{CH}_3\text{COCH}_2\text{Cl}] = 5 \cdot 10^{-4}$ mol l$^{-1}$.

<table>
<thead>
<tr>
<th>$\lambda$ / nm</th>
<th>A (Cl)</th>
<th>t / ns</th>
<th>$10^6 c_0$ (Cl) mol l$^{-1}$</th>
<th>$10^6 c_{t=0}$ (Cl) mol l$^{-1}$</th>
<th>$10^{-16}$ N (Cl)</th>
<th>$W_{\text{LASER}}$ / mJ</th>
<th>$10^{-17}$N$_{\text{ABS}}$</th>
<th>$\Phi$</th>
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<td>275</td>
<td>0.071</td>
<td>50</td>
<td>0.99</td>
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<td>290</td>
<td>1.012</td>
<td>0.171</td>
</tr>
<tr>
<td>280</td>
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<td>50</td>
<td>1.00</td>
<td>1.03</td>
<td>1.73</td>
<td>290</td>
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<td>0.176</td>
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<td>1.012</td>
<td>0.166</td>
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Annex I  Thermochemistry of the photodissociation processes in aqueous solution

In order to obtain the excess energies for the different systems, it is necessary to know the bond dissociation energy (BDE) of the X-O$^{-}$ bonds in the precursors molecules. In the systems where no anions are formed (e.g., H$_2$O$_2$, HONO and HOCl), the gas phase BDEs have been considered. For all the other systems where one or both of the fragments are anions the BDEs must be calculated and in the case of the oxy-anions these represent the bond energies of the reaction enthalpies for the reactions:

\[ X\text{O}_{n}^{-} \rightarrow X\text{O}_{n-1}^{-} + O^{-} \]  \hspace{1cm} (R-I)

Whereas for the photolysis of the sulphuroxyl anions,

\[ S\text{O}_8^{2-} \rightarrow 2 \text{SO}_4^{-} \]  \hspace{1cm} (R-II)

As well as

\[ S\text{O}_6^{2-} \rightarrow 2 \text{SO}_3^{-} \]  \hspace{1cm} (R-III)

The aqueous phase standard enthalpies of formation (\(\Delta H_{f}^{0}(\text{aq})\)) for all the treated species are known\textsuperscript{12}. Furthermore, the gas phase standard enthalpies of formation (\(\Delta H_{f}^{0}(\text{g})\)) for all the neutral substrate and products as well as for most of the anions are also existing\textsuperscript{13}. The thermochemistry of several dissociation processes of oxy anions has been discussed with a cyclic process by Friedman\textsuperscript{14}. This cyclic process is depicted in Figure I.
Figure S2: Thermochemistry of the photodissociation of oxy-anions after Friedman$^{14}$. 

From the thermodynamic treatment after Friedman as well as the following work of Treinin (1970)$^{15}$ it follows that the reaction enthalpy ($\Delta H_R$) for the reactions like:

$$\text{XO}_n^-\text{(aq)} + \text{H}_2\text{O}\text{(l)} \rightarrow \text{XO}_{n-1}\text{(aq)} + \text{OH}\text{(aq)} + \text{OH}^-\text{(aq)} \quad \text{(R-IV)}$$

It can be represented and calculated as the sum of R-V:

$$\text{XO}_n^- \rightarrow \text{XO}_{n-1} + \text{O}^- \quad \text{(R-I)}$$

And the reaction of O$^-$ with the water, e.g.

$$\text{O}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{OH} \quad \text{(R-V)}$$
However, the reaction enthalpy for the reaction (R-V) can be calculated only for the gas phase since the aqueous phase formation enthalpy ($\Delta H_f^{(aq)}$) of O- radical anion is not known. From the gas phase data a value of reaction enthalpy for reaction (R-V) of $\Delta H^\circ_{R}(R-V) = 38.095$ kJ mol$^{-1}$ is given, so that the reaction enthalpy for (R-I) can be calculated as follow:

\[
BDE = \Delta H^\circ_{R} (R-I) = \Delta H^\circ_{R} (R-IV) - \Delta H^\circ_{R} (R-V)
\]

Whereas the Treinin values have been considered for the reaction enthalpy of the reactions like (R-IV)$^{15}$. The obtained values have been summarised in Table IX.

The gas phase BDEs have been applied for in the case of HOX with X= OH, Cl, NO.

For the peroxyl energy bond in the peroxomonosulphate anion (HSO$_5^-$) the value of BDE = 377 kJ mol$^{-1}$ given by Benson $^{16}$ has been considered. A BDE of 92 kJ mol$^{-1}$ is given for the peroxyl bond in the H$_2$S$_2$O$_8$ molecule, which has been also applied for the peroxodisulphate anion. A thermochemical calculation for this bond leads to a BDE (O)S-OO-2SO$_3^-$ = 93 kJ mol$^{-1}$, in which the standard entropy of formation $\Delta S^\circ_f$ has been assumed equivalent to the one of the sulphate radical anion (SO$_4^{2-}$) ($\Delta S^\circ_f$ (SO$_4^{2-}$) = 20.8 J mol$^{-1}$ K$^{-1}$)$.^{12}$). The good agreement obtained with the Benson value shows the validity of the taken approximation.

No BDE is available for the S-S bond in the dithionate anion, therefore an estimation have been done. The Gibbs free energy of of formation (\(\Delta G_f^0\)) for S$_2$O$_6^{2-}$ and SO$_3^-$ are $\Delta G_f^0$(S$_2$O$_6^{2-}$) = -960 kJ mol$^{-1}$ and $\Delta G_f^0$(SO$_3^-$) = -426 kJ mol$^{-1}$, respectively $^{12}$. A similar approximation to the case of sulphate radical anion has been taken and a $\Delta S^\circ_f$ (SO$_3^-$) = $\Delta S^\circ_f$ (SO$_4^{2-}$) = -293 J mol$^{-1}$ K$^{-1}$ $^{12}$ have been applied. The aqueous phase $\Delta S^\circ_f$ of dithionate anion is also not known and it has been estimated equal to $\Delta S^\circ_f$ (S$_2$O$_6^{2-}$) = 160 J mol$^{-1}$ K$^{-1}$ as average value between S$_2$O$_4^{2-}$ und S$_2$O$_8^{2-}$ values $^{12}$. Applying the Gibbs-Helmholtz relationship, the bond dissociation energy of S-S bond in the dithionate anion has been calculated as follow:

\[
BDE (\text{O}_3\text{S-SO}_3^-) = 2 \cdot \Delta G_f^0(\text{SO}_3^-) - \Delta G_f^0(S_2\text{O}_6^{2-}) - \frac{298}{1000} \cdot (2 \cdot \Delta S_f^0 (\text{SO}_3^-) - \Delta S_f^0 (S_2\text{O}_6^{2-}))
\]

(II)
It follows a value of BDE \((O_2S-SO_3^-) = 173 \text{ kJ mol}^{-1}\). This results is in good agreement with suggestion of Waygood und McElroy, whose indicated that the BDE of the S-S-bond in \(S_2O_6^{2-}\) should be double respect to the BDE of the peroxyl bond in \(S_2O_8^{2-}\).  

**Table S9:** Applied bond dissociation energies (BDEs, kJ mol\(^{-1}\))

<table>
<thead>
<tr>
<th>Precursor XO(_n)(^-)</th>
<th>BDE(XO(_{n-1})-O(^-)) /kJ mol(^{-1})</th>
<th>Measurement / Ref.</th>
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<tr>
<td>NO(_2^-)</td>
<td>192</td>
<td>This work, see text</td>
</tr>
<tr>
<td>NO(_3^-)</td>
<td>217</td>
<td>This work, see text</td>
</tr>
<tr>
<td>ClO(^-)</td>
<td>230</td>
<td>This work, see text</td>
</tr>
<tr>
<td>ClO(_2^-)</td>
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<td>This work, see text</td>
</tr>
<tr>
<td>Precursor XOH</td>
<td>BDE(X-OH) /kJ mol(^{-1})</td>
<td>Measurement / Ref.</td>
</tr>
<tr>
<td>H(_2)O(_2)</td>
<td>213 ± 4</td>
<td>Gas phase, [12]</td>
</tr>
<tr>
<td>HOCl</td>
<td>251 ± 13</td>
<td>Gas phase, [12]</td>
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<tr>
<td>HONO</td>
<td>206</td>
<td>Gas phase, [12]</td>
</tr>
<tr>
<td>HSO(_5^-)</td>
<td>377</td>
<td>Benson, [16]</td>
</tr>
<tr>
<td>Precursor [(XO(_n))^2(^-)]</td>
<td>BDE(XO(_n)-XO(_n))^(-) /kJ mol(^{-1})</td>
<td>Measurement / Ref.</td>
</tr>
<tr>
<td>(S_2O_8^{2-})</td>
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<td>Benson, [16]</td>
</tr>
<tr>
<td>(S_2O_6^{2-})</td>
<td>173</td>
<td>This work, see text</td>
</tr>
</tbody>
</table>

From the obtained BDEs the total excess energy can then be calculated as:

\[
W_{\text{exc}} = W(\nu) - \text{BDE} \quad [\text{kJ mol}^{-1}] \quad (\text{III})
\]
Annex References