

## Oxidation of chloride by sulfate radicals

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### Introduction

As highly reactive species sulfate radicals ( $\text{SO}_4^{\bullet-}$ ) are principally capable of degrading pollutants such as arsenic<sup>1</sup>, trichloroethene<sup>2</sup>, *tert*-butylmethylether<sup>3</sup>, chlorinated ethenes<sup>4</sup> and phenols<sup>5</sup>. Thus,  $\text{SO}_4^{\bullet-}$  based oxidation is frequently discussed as an alternative oxidative treatment option for pollutant control in water treatment. Conventional radical based processes are based on nonselective hydroxyl radicals ( $\bullet\text{OH}$ ) (advanced oxidation process (AOP)). Due to the different nature of  $\bullet\text{OH}$  and  $\text{SO}_4^{\bullet-}$ ,  $\text{SO}_4^{\bullet-}$  may have a potential to overcome limitations of conventional AOP. A case in point are perfluorinated compounds which are inert towards  $\bullet\text{OH}$ <sup>6-8</sup> but slightly reactive towards  $\text{SO}_4^{\bullet-}$ <sup>6</sup>.  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  can be formed in a photochemical way by cleavage of the peroxide-bonding in  $\text{S}_2\text{O}_8^{2-}$  and  $\text{H}_2\text{O}_2$ , respectively. Both peroxides have similar photochemical features such as molar absorption ( $\epsilon_{254}(\text{H}_2\text{O}_2) = 20 \text{ cm}^{-1}$ <sup>9</sup>,  $\epsilon_{254}(\text{S}_2\text{O}_8^{2-}) = 22 \text{ cm}^{-1}$ <sup>10</sup>) and quantum yield of radical formation  $\Phi_{254}(\text{H}_2\text{O}_2) = 1 \text{ mol einstein}^{-1}$ <sup>11</sup>,  $\Phi_{254}(\text{S}_2\text{O}_8^{2-}) = 1.4 \text{ mol einstein}^{-1}$ <sup>12, 13</sup>. Thus, reactor design for photolysis of  $\text{H}_2\text{O}_2$  (UV/ $\text{H}_2\text{O}_2$ ) which is already applied in water treatment (e.g., Andijk (Netherlands), City of Cornwall (Canada) and Orange County water district (USA)) would principally suit for UV/ $\text{S}_2\text{O}_8^{2-}$  and investment costs might be justifiable.

Main constituents of source water, i.e., dissolved organic carbon (DOC), and inorganic ions such as  $\text{HCO}_3^-/\text{CO}_3^{2-}$  largely affect the efficiency of radical based water treatment. However, a systematic investigation regarding the influence of main constituents in natural waters is hardly available with respect to  $\text{SO}_4^{\bullet-}$  based oxidation. One important reaction is  $\text{SO}_4^{\bullet-}$  plus  $\text{Cl}^-$  ( $k = 2.8 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ <sup>14</sup>), since  $\text{Cl}^-$  is typically present in mM concentrations in natural waters. However, the reaction  $\text{SO}_4^{\bullet-}$  plus  $\text{Cl}^-$  gives rise to chlorine atoms ( $\text{Cl}^\bullet$ ) as primary products which induce a sequence of reactions involving water and  $\text{Cl}^-$  as main reactants. Corresponding equilibria have been investigated in detail<sup>14-16</sup> revealing that  $\bullet\text{OH}$  are formed in these reactions. Beside  $\bullet\text{OH}$  the reactions might also yield  $\text{ClO}_3^-$ , especially at acidic conditions. The presence of  $\text{ClO}_3^-$  is undesired in drinking water, since it is classified as being harmful to human health and ecosystems (EU regulation 1907/2006; note that Switzerland established a drinking water standard of  $200 \mu\text{gL}^{-1}$ <sup>17</sup> and WHO recommended a maximum value of  $700 \mu\text{gL}^{-1}$  (WHO/SDE/WSH/05.08/86)).

For deciding if UV/ $\text{S}_2\text{O}_8^{2-}$  is a useful option in water treatment the influence of  $\text{Cl}^-$  is a very important issue and has to be carefully investigated. The present study comprises a thorough investigation of  $\text{ClO}_3^-$  formation in UV/ $\text{S}_2\text{O}_8^{2-}$  in pure water including a model of its formation.

## Methods

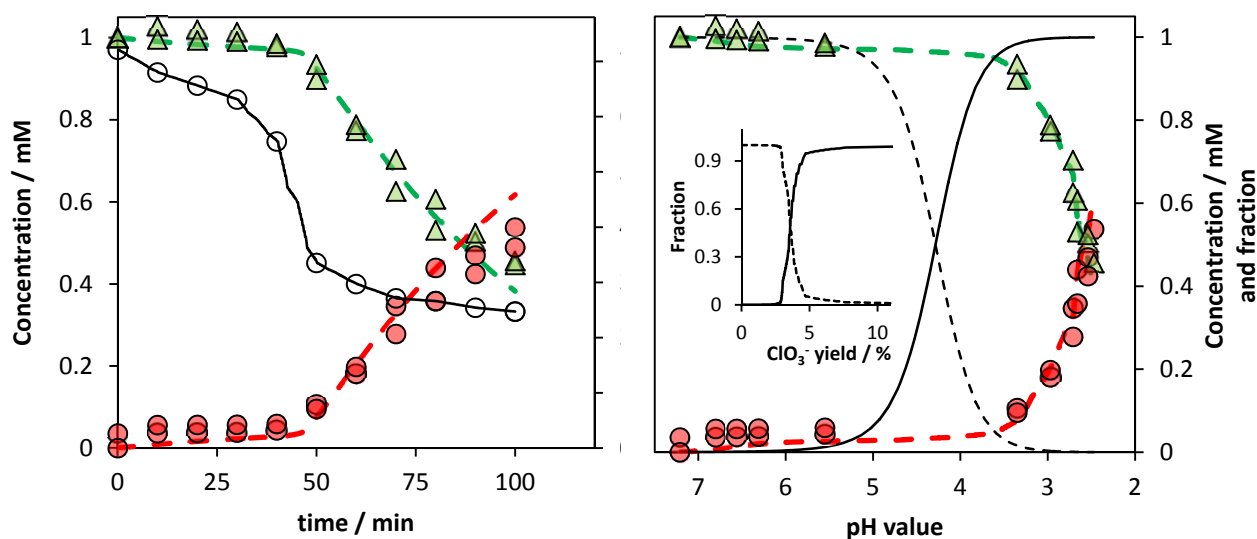
Sulfate radicals were generated by photolysis of peroxodisulfate (UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) in a merry-go-round apparatus equipped with a low pressure mercury lamp. This radiation source emits monochromatic light at 254 nm (Heraeus Noble Light GPH303T5L/4, 15 W). The reactions were buffered with phosphate. pH adjustments were done by addition of sulfuric acid or sodium hydroxide, respectively. Methanol was added to the samples (1 M in the sample) for scavenging low levels of SO<sub>4</sub><sup>•-</sup> which could be formed during storage time. Cl<sup>-</sup> was analyzed by ion chromatography (Metrohm 883 basic) equipped with a conductivity detector coupled with ion suppression (anion separation column with quaternary ammonium groups: Metrosep A Supp 4 - 250/4.0 mm, particle size 9 μm; eluent HCO<sub>3</sub><sup>-</sup> (1.7 mM), CO<sub>3</sub><sup>2-</sup> (1.8 mM) mixed with acetonitrile (30%); flow: 1 mL min<sup>-1</sup>; retention time 3.8 min).

For determining the fluence rate, chemical actinometry was performed using uridin as actinometer as described by von Sonntag<sup>18</sup>. The internal filter effect by UV-absorption of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> has been corrected by the Morowitz correction factor<sup>19</sup>. For calculating the SO<sub>4</sub><sup>•-</sup>-formation rate in UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> a quantum yield of 1.4 mole Einstein<sup>-1</sup><sup>12, 13</sup> and a molar absorption (254 nm) of 22 cm<sup>-1</sup> was used.

## Results and discussion

Figure 1 shows a comparison of determined and modeled product patterns in the oxidation of Cl<sup>-</sup> in UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. During the experiment the solution acidifies, which is included in the model calculations. In the investigated system no Cl<sup>-</sup> turnover can be observed at pH ≥ 6. However, at lower pH values Cl<sup>-</sup> is oxidized yielding ClO<sub>3</sub><sup>-</sup> nearly quantitatively. The corresponding mechanism can be proposed as follows:

SO<sub>4</sub><sup>•-</sup> reacts with Cl<sup>-</sup> giving rise to SO<sub>4</sub><sup>2-</sup> and Cl<sup>•</sup> (reaction 1). It has been suggested that Cl<sup>•</sup> forms complexes with water (H<sub>2</sub>OCl<sup>•</sup>)<sup>14, 20, 21</sup>, which may act as an oxygen acid (pK<sub>a</sub> 5.1<sup>22</sup>), and deprotonate (reaction 4 and 9) yielding <sup>•</sup>OH. At a Cl<sup>-</sup> concentration of 1 mM, a substantial amount of Cl<sup>•</sup> may also react with Cl<sup>-</sup> and Cl<sub>2</sub><sup>•-</sup> is formed (reaction 3). Cl<sub>2</sub><sup>•-</sup> may react with water (reaction 6) giving rise to HClO<sup>•-</sup>, the precursor of <sup>•</sup>OH or Cl<sup>•</sup> (reaction 8 and 9). Formation of <sup>•</sup>OH is predominant at neutral pH whereas Cl<sup>•</sup> concentration increases at low pH values (see below). Cl<sub>2</sub><sup>•-</sup> may also recombine yielding Cl<sub>2</sub> and Cl<sup>-</sup> (reaction 7). Cl<sub>2</sub> hydrolyses to form HOCl/OCl<sup>-</sup> which will be further oxidized by <sup>•</sup>OH or Cl<sup>•</sup> giving rise to ClO<sub>3</sub><sup>-</sup> (reaction 10). In this sequence of reactions the formation of Cl<sub>2</sub> largely depends on steady state concentration of Cl<sup>•</sup>. The concentration of Cl<sup>•</sup> in turn is related to the apparent equilibrium in reaction 4. With decreasing pH this equilibrium is shifted towards Cl<sup>•</sup> thus, enhancing ClO<sub>3</sub><sup>-</sup> formation. At a pH-value of ≈ 3.4 the Cl<sup>-</sup> turnover approaches the maximum rate.



**Figure 1: Oxidation of  $\text{Cl}^-$  by  $\text{SO}_4^{\bullet-}$  at decreasing pH value in pure water;  $\text{Cl}^-$ : green triangles,  $\text{ClO}_3^-$ : red circles; a) concentration of  $\text{Cl}^-$  and  $\text{ClO}_3^-$  as well as pH (open circles) vs. time, model predictions: dashed line; b) concentration of  $\text{Cl}^-$  and  $\text{ClO}_3^-$  vs. pH value; black lines give the fractions of  $\bullet\text{OH}$  (dashed) and  $\text{Cl}\bullet$  (solid) involved in oxidation of  $\text{HOCl}/\text{OCl}^-$ ; inset: fraction of  $\bullet\text{OH}$  (dashed) and  $\text{Cl}\bullet$  (solid) involved in oxidation of  $\text{HOCl}/\text{OCl}^-$  vs.  $\text{ClO}_3^-$  yield;  $[\text{Cl}^-]_0 = 1 \text{ mM}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 10 \text{ mM}$ ,  $[\text{phosphate}] = 10 \text{ mM}$ ; fluence rate =  $62 \pm 2 \mu\text{Einstein m}^{-2}\text{s}^{-1}$**

However, at  $\text{pH} \geq 6$  no consumption of  $\text{Cl}^-$  or formation of  $\text{ClO}_3^-$  has been observed in  $\text{UV}/\text{S}_2\text{O}_8^{2-}$  (note that  $\text{Cl}\bullet$  still forms  $\text{HOCl}\bullet^-$  (reaction 4) which decomposes to  $\bullet\text{OH}$  and  $\text{Cl}^-$  (reaction 9)). Figure 1b shows the fraction of  $\bullet\text{OH}$  and  $\text{Cl}\bullet$  reacting with  $\text{HOCl}/\text{OCl}^-$  as a function of pH which has been derived from the model calculations. It can be seen, that  $\bullet\text{OH}$  possibly contribute in the oxidation of  $\text{HOCl}/\text{OCl}^-$  at pH values  $> 4$ . However, at lower pH values this reaction is suppressed by speciation since  $\text{HOCl}$  largely dominates over  $\text{OCl}^-$  and has been considered being not reactive towards  $\bullet\text{OH}$  in the model calculations. The model well reflects the experimental data neglecting the reaction  $\bullet\text{OH}$  plus  $\text{HOCl}$ , indicating that the corresponding reaction indeed plays a minor role.  $\text{Cl}\bullet$  reacts with both  $\text{HOCl}$  and  $\text{OCl}^-$  at a similar rate (Table 1), thus the reaction with  $\text{HOCl}/\text{OCl}^-$  is nearly independent of pH. Since formation of  $\text{HOCl}/\text{OCl}^-$  is favored at acidic conditions below its  $\text{pK}_a$  value, oxidation of  $\text{HOCl}/\text{OCl}^-$  is mainly driven by  $\text{Cl}\bullet$ . After a  $\text{Cl}^-$  turnover into  $\text{ClO}_3^-$  of 5% the fraction of the reaction  $\bullet\text{OH}$  plus  $\text{HOCl}/\text{OCl}^-$  is negligible ( $< 5\%$ ) (see inset of Figure 1b). Oxidation of  $\text{HOCl}/\text{OCl}^-$  by  $\text{Cl}\bullet$  (or  $\bullet\text{OH}$ ) gives  $\text{ClO}\bullet$  which disproportionates in its reaction with water yielding  $\text{ClO}^-$  and  $\text{ClO}_2^-$  (reaction 13). The oxidation of  $\text{ClO}_2^-$  may be driven by  $\bullet\text{OH}$  yielding the final product  $\text{ClO}_3^-$  (reaction 17). Some additional reactions are also included in the model calculation.  $\text{H}_2\text{O}_2$  could be formed by recombination of  $\bullet\text{OH}$  (reaction 16).  $\text{H}_2\text{O}_2$  might act as a  $\bullet\text{OH}$  radical scavenger giving rise to the reducing radical  $\text{HO}_2\bullet$ . In fact  $\text{HO}_2\bullet$  rapidly reacts with  $\text{Cl}_2^{\bullet-}$  giving rise to  $\text{Cl}^-$  (reaction 18) which could reduce the  $\text{ClO}_3^-$  formation rate. However, model calculations are not significantly influenced by reaction 18.

The presented results indicate that under typical conditions of water treatment ( $\text{pH} > 6$ ) formation of  $\text{ClO}_3^-$  is not likely to happen. However, in remediation of ground waters

where  $S_2O_8^{2-}$  finds increasing application, residence time might be sufficient to cause a considerable acidification in turn of reactions of  $SO_4^{\bullet-}$  with  $Cl^-$  or other reactions releasing protons. Without any option of controlling the reaction in the subsurface, acidification may have several adverse effects such as formation of  $ClO_3^-$ , mobilization of metals and formation of chlorinated compounds. The latter may arise from increasing steady state concentrations of reactive chlorine species.

**Table 1: Reactions involved in the oxidation of  $Cl^-$  during UV/ $S_2O_8^{2-}$**

No.	Reaction	Reaction rate forward			Reaction rate backward		
(1)	$SO_4^{\bullet-} + Cl^- \rightleftharpoons Cl^{\bullet} + SO_4^{2-}$	$k = 2.7 \times 10^8$	$M^{-1}s^{-1}$ <sup>14</sup>		$k = 2.5 \times 10^8$	$M^{-1}s^{-1}$	<sup>23</sup>
(2)	$2 SO_4^{\bullet-} \rightarrow S_2O_8^{2-}$	$k = 4.4 \times 10^8$	$M^{-1}s^{-1}$ <sup>24</sup>				
(3)	$Cl^{\bullet} + Cl^- \rightleftharpoons Cl_2^{\bullet-}$	$k = 8 \times 10^9$	$M^{-1}s^{-1}$ <sup>25</sup>		$k = 4.7 \times 10^4$	$s^{-1}$	<sup>14</sup>
(4)	$Cl^{\bullet} \rightleftharpoons HOCl^{\bullet-} + H^+$	$k = 2.5 \times 10^5$	$M^{-1}s^{-1}$ <sup>15</sup>		$k = 2.1 \times 10^{10}$	$M^{-1}s^{-1}$	<sup>26</sup>
(5)	$Cl^{\bullet} + OH^- \rightarrow \bullet OH + Cl^-$	$k = 1.8 \times 10^{10}$	$M^{-1}s^{-1}$ <sup>27</sup>				
(6)	$Cl_2^{\bullet-} + H_2O \rightarrow HOCl^{\bullet-} + Cl^- + H^+$	$k = 1.3 \times 10^3$	$s^{-1}$ <sup>28</sup>				
(7)	$Cl_2^{\bullet-} + Cl_2^{\bullet-} \rightarrow Cl_2 + 2Cl^-$	$k = 2.1 \times 10^9$	$M^{-1}s^{-1}$ <sup>29</sup>				
(8)	$Cl_2^{\bullet-} + OH^- \rightarrow ClOH^- + Cl^-$	$k = 4.5 \times 10^7$	$M^{-1}s^{-1}$ <sup>29</sup>				
(9)	$ClOH^{\bullet-} \rightleftharpoons \bullet OH + Cl^-$	$k = 6.1 \times 10^9$	$s^{-1}$ <sup>26</sup>		$k = 4.3 \times 10^9$	$M^{-1}s^{-1}$	<sup>26</sup>
(10)	$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+$	$k = 5.5$	$s^{-1}$ <sup>30</sup>				
(11)	$HOCl \rightleftharpoons H^+ + OCl^-$	$pKa\ 7.42$		<sup>31</sup>			
(12)	$ClO^- + \bullet OH \rightarrow ClO^{\bullet} + OH^-$	$k = 9 \times 10^9$	$M^{-1}s^{-1}$ <sup>32</sup>				
(13)	$2ClO^{\bullet} + H_2O \rightarrow ClO^- + ClO_2^- + 2H^+$	$k = 2.5 \times 10^9$	$M^{-1}s^{-1}$ <sup>22</sup>				
(14)	$ClO_2^- + \bullet OH \rightarrow ClO_2^{\bullet} + OH^-$	$k = 4.2 \times 10^9$	$M^{-1}s^{-1}$ <sup>33</sup>				
(15)	$ClO_2^{\bullet} + \bullet OH \rightarrow ClO_3^- + H^+$	$k = 4 \times 10^9$	$M^{-1}s^{-1}$ <sup>33</sup>				
(16)	$\bullet OH + \bullet OH \rightarrow H_2O_2$	$k = 5.5 \times 10^9$	$M^{-1}s^{-1}$ <sup>34</sup>				
(17)	$H_2O_2 + OH^- \rightarrow HO_2^{\bullet} + H_2O$	$k = 2.7 \times 10^7$	$M^{-1}s^{-1}$ <sup>35</sup>				
(18)	$HO_2^{\bullet} + Cl_2^{\bullet-} \rightarrow 2Cl^- + O_2 + H^+$	$k = 4.5 \times 10^9$	$M^{-1}s^{-1}$ <sup>36</sup>				
(19)	$Cl^{\bullet} + ClO^- \rightarrow ClO^{\bullet} + Cl^-$	$k = 8.0 \times 10^9$	$M^{-1}s^{-1}$ <sup>22</sup>				
(20)	$Cl^{\bullet} + HOCl \rightarrow ClO^{\bullet} + Cl^- + H^+$	$k = 3.0 \times 10^9$	$M^{-1}s^{-1}$ <sup>22</sup>				

At typical conditions of drinking water treatment the reaction of  $SO_4^{\bullet-}$  plus  $Cl^-$  mainly yields  $\bullet OH$ , rendering this process into a conventional AOP. However, alkalinity interrupts this process by scavenging of  $Cl^{\bullet}$  ( $k(Cl^{\bullet} + HCO_3^-) = 2.2 \times 10^8\ M^{-1}s^{-1}$ <sup>37</sup>), thus reducing the oxidation efficiency. The energy demand for 90% degradation of atrazine in River Ruhr water (alkalinity = 2.07 mM, DOC = 2.45,  $Cl^-$  = 1.05 mM) has been determined for UV/ $S_2O_8^{2-}$ , UV/ $H_2O_2$  and ozonation. The energy efficiency of UV/ $S_2O_8^{2-}$  hardly differed from UV/ $H_2O_2$  ( $\approx 0.9\ kWh$ ) and ozonation was much more efficient than both UV-based processes ( $0.06\ kWhm^{-3}$ ). In sum UV/ $S_2O_8^{2-}$  hardly reveal any benefit over conventional AOP such as UV/ $H_2O_2$ , neither in degrading  $\bullet OH$  recalcitrant compounds nor in energy demand. Thus, the application of  $SO_4^{\bullet-}$  based process as a water treatment option has to be carefully scrutinized.

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