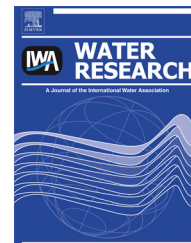


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Formation of bromate in sulfate radical based oxidation: Mechanistic aspects and suppression by dissolved organic matter

Holger V. Lutze^{a,c,*}, Rani Bakkour^a, Nils Kerlin^a, Clemens von Sonntag^{a,b},
Torsten C. Schmidt^{a,c,d}

^a University Duisburg-Essen, Instrumental Analytical Chemistry, Universitätsstr. 5, D-45141 Essen, Germany

^b Max-Planck-Institut für Strahlenchemie, Stiftstr. 34-36, Mülheim an der Ruhr, Germany

^c IWW Water Centre, Moritzstr. 26, D-45476 Mülheim an der Ruhr, Germany

^d University Duisburg-Essen, Centre for Water and Environmental Research (ZWU), Universitätsstr. 2, D-45141 Essen, Germany

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ABSTRACT

Sulfate radical based oxidation is discussed being a potential alternative to hydroxyl radical based oxidation for pollutant control in water treatment. However, formation of undesired by-products, has hardly been addressed in the current literature, which is an issue in other oxidative processes such as bromate formation in ozonation of bromide containing water (US-EPA and EU drinking water standard of bromate: $10 \mu\text{g L}^{-1}$). Sulfate radicals react fast with bromide ($k = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) which could also yield bromate as final product. The mechanism of bromate formation in aqueous solution in presence of sulfate radicals has been investigated in the present paper. Further experiments were performed in presence of humic acids and in surface water for investigating the relevance of bromate formation in context of pollutant control. The formation of bromate by sulfate radicals resembles the well described mechanism of the hydroxyl radical based bromate formation. In both cases hypobromous acid is a requisite intermediate. In presence of organic matter formation of bromate is effectively suppressed. That can be explained by formation of superoxide formed in the reaction of sulfate radicals plus aromatic moieties of organic matter, since superoxide reduces hypobromous acid yielding bromine atoms and bromide. Hence formation of bromate can be neglected in sulfate radical based oxidation at typical conditions of water treatment.

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1. Introduction

Oxidative water treatment based on highly reactive hydroxyl radicals ($\cdot\text{OH}$) is referred to as advanced oxidation processes (AOP) and can be used for degrading recalcitrant pollutants

such as pesticides, X-ray contrast media and fuel additives (e.g., MTBE) (von Gunten, 2003a). $\cdot\text{OH}$ can be generated in various ways e.g., by photolysis of hydrogen peroxide (UV/ H_2O_2) (Legrini et al., 1993) or in ozonation (von Gunten, 2003a). Beside $\cdot\text{OH}$, sulfate radicals ($\text{SO}_4^{\cdot-}$) are frequently investigated

* Corresponding author. University Duisburg-Essen, Instrumental Analytical Chemistry, Universitätsstr. 5, D-45141 Essen, Germany. Tel.: +49 201 183 6791.

E-mail address: holger.lutze@uni-due.de (H.V. Lutze).

as potential alternative oxidants for water treatment (Anipsitakis and Dionysiou, 2003, 2004; Anipsitakis et al., 2006; Hori et al., 2004, 2008, 2005; Kutsuna and Hori, 2007; Liang et al., 2008, 2007; Manoj et al., 2007) and have already been applied in ground water remediation (Siegrist et al., 2011). $\text{SO}_4^{\cdot-}$ can be formed in various ways using $\text{S}_2\text{O}_8^{2-}$ as a radical precursor. One possibility is its photolysis by UVC-radiation ($\text{UV}/\text{S}_2\text{O}_8^{2-}$) which is in analogy to $\text{UV}/\text{H}_2\text{O}_2$. A major drawback in oxidative water treatment is the formation of undesired by-products. Ozone based processes, for instance, can be limited by the formation of bromate (BrO_3^-) a potential carcinogen (US-EPA and EU drinking water standard: $10 \mu\text{g L}^{-1}$) arising from the oxidation of Br^- (von Gunten, 2003b). Thereby, formation of BrO_3^- can be driven by O_3 and/or $\cdot\text{OH}$. Corresponding mechanisms have already been discussed in detail (Haag and Hoigné, 1983; von Gunten, 2003b; von Gunten and Hoigne, 1994; von Gunten and Oliveras, 1998). For reactions in which solely O_3 or $\cdot\text{OH}$ are involved, hypobromous acid (HOBr) is a requisite intermediate. At typical conditions of water treatment HOBr can effectively be reduced by hydrogen peroxide (H_2O_2) yielding Br^- (von Gunten and Oliveras, 1997). This instance is used for mitigating BrO_3^- formation in ozone applications by addition of H_2O_2 (von Gunten, 2003b). In most $\cdot\text{OH}$ based processes H_2O_2 is used as a radical source (e.g., $\text{UV}/\text{H}_2\text{O}_2$), thus preventing BrO_3^- formation. UV/TiO_2 is known to not require H_2O_2 to form $\cdot\text{OH}$. However, studies indicated that BrO_3^- is not formed in this process (Tercero Espinoza and Frimmel, 2008). Also gamma radiolysis which is discussed being a potential water treatment option for both, disinfection (de Souza et al., 2011) and pollutant degradation (Dessouki et al., 1999; Getoff, 2002; Tahri et al., 2010) might oxidize Br^- yielding BrO_3^- . In analogy to $\cdot\text{OH}$ the reaction of $\text{SO}_4^{\cdot-}$ plus Br^- ($k = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Redpath and Willson, 1975)) yield BrO_3^- (Fang and Shang, 2012). In the recent work of Fang and Shang (2012) an empirical model has been established, which was used for describing the formation of HOBr/OBr^- and BrO_3^- . This approach has been extended in our work by a mechanistic discussion. The present study provides a reaction mechanism based on data available in the literature for developing a kinetic model of $\text{SO}_4^{\cdot-}$ driven formation of BrO_3^- . This model has been used to describe the behavior of HOBr and BrO_3^- in the oxidation of Br^- which was experimentally determined at various conditions. Furthermore, the potential of BrO_3^- formation in natural matrices has been investigated and contrasted to the oxidation strength available for pollutant control.

2. Methods

All chemicals were commercially available and used as received.

Acetonitrile ($\geq 99.9\%$) Sigma Aldrich, atrazine ($\geq 97.4\%$) Riedel-de Haën, 4-chlorobenzoic acid (pCBA) (99%) Aldrich, hydrochloric acid (37% in water, p.a.) Merck, hydrogen peroxide (30%) Sigma Aldrich, methanol (p.a.) Sigma–Aldrich, 4-nitrobenzoic acid (pNBA) ($\geq 97.4\%$) Sigma Aldrich, oxygen ($\geq 99.9\%$) Liquid Air, phosphoric acid ($\geq 85\%$) Merck, potassium bromate (99.5%) Fluka, potassium chloride ($\geq 99.5\%$) Riedel-de Haën, pure water has been prepared by treating deionized water with a pure lap ultra instrument (Elga) (electrical resistance $18.6 \text{ M}\Omega$), sodium

bicarbonate ($\geq 99.5\%$) KMF optichem, sodium bromate (99%) Fluka, sodium carbonate ($\geq 99.8\%$) Riedel-de Haën, sodium hydroxide ($\geq 99.9\%$, p.a.) VWR, sodium peroxodisulfate (p.a.) Sigma–Aldrich, sulfuric acid (95–97%) Applichem International, Suwannee River NOM (reverse osmosis concentrate) International Humic Acid Society, Uridine ($\geq 99\%$) Sigma.

Sulfate radicals were generated by photolysis of peroxodisulfate ($\text{UV}/\text{S}_2\text{O}_8^{2-}$) 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 (185 nm band suppressed)). The fluence rate has been determined by uridine actinometry according to von Sonntag and Schuchmann (1992). Solutions were buffered with phosphate. Even though $\text{SO}_4^{\cdot-}$ reacts with HPO_4^{2-} with a considerable rate ($k = 1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) (H_2PO_4^- is nearly inert ($k < 7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$)) the reactions under study are faster by several orders of magnitudes ($k(\text{SO}_4^{\cdot-} \text{ plus } \text{Br}^-) = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). This allows addition of phosphate buffer in excess over bromide (e.g., factor 100), which is necessary for keeping pH constant (experimental details can be found in the caption of corresponding figures). pH-adjustments have been 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 $\text{SO}_4^{\cdot-}$ which may be formed during storage time by thermolysis of $\text{S}_2\text{O}_8^{2-}$. BrO_3^- and Br^- were 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 $9 \mu\text{m}$; eluent HCO_3^- (1.7 mM), CO_3^{2-} (1.8 mM) mixed with acetonitrile (30% (v/v)); flow: 1 mL min^{-1} ; retention times: Br^- : 3.6 min, BrO_3^- : 4.4 min). For determining BrO_3^- and Br^- at concentrations in the μM range a different IC system has been used coupled with ion- and subsequent CO_2 -suppression (Metrohm, 881 Compact IC plus), equipped with a high capacity anion separation column (Metrosep A Supp 5–250/4.0, particle size $5 \mu\text{m}$) which was necessary for separation of Cl^- and BrO_3^- (Eluent: 3.2 mM Na_2CO_3 and 1.0 mM NaHCO_3 , flow: 0.7 mL min^{-1} ; retention times: BrO_3^- : 8.0 min, Cl^- : 8.7 min, Br^- : 13.0 min). For determining Br^- and BrO_3^- in River Ruhr water an IC-ICP-MS system has been used (200 Series from Perkin Elmer, Eluent: 10 mM NaOH, flow: 1.8 mL min^{-1}). Atrazine, 4-chlorobenzoic acid (pCBA) and 4-nitrobenzoic acid (pNBA) have been determined by HPLC with UV-detection (Shimadzu) (C18 reversed phase separation column: Bischoff, NUCLEOSIL 100, 250/4.0 mm, particle size: $5.0 \mu\text{m}$). As eluent a gradient of methanol/water has been used (gradient program (methanol content (v/v)): 0–3 min: gradient 20–50%, 3–25 min: gradient 50–75%; 25–30 min: gradient 75–20%, 30–38 min: isocratic 20%; flow 0.6 mL min^{-1} ; retention times/measured wave length: pNBA: 20.6 min/262 nm; atrazine: 25.8 min/234 nm, pCBA: 26.5 min/234 nm). HOBr has been determined by UV-absorption as OBr^- at 329 nm ($\epsilon(\text{OBr}^-) = 332 \text{ M}^{-1} \text{ cm}^{-1}$ (Troy and Margerum, 1991)) by adjusting the solution to pH 11. Model calculations have been performed by using the software tool Kintecus (Ianni, 2008) (quantum yields for radical formation and molar absorption coefficients of peroxodisulfate can be obtained from Mark et al., 1990).

Experiments in presence of humic acids were performed for simulating bromate formation in a real water during UV/

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