



# Reaction of bromine and chlorine with phenolic compounds and natural organic matter extracts – Electrophilic aromatic substitution and oxidation



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## ABSTRACT

Phenolic compounds are known structural moieties of natural organic matter (NOM), and their reactivity is a key parameter for understanding the reactivity of NOM and the disinfection by-product formation during oxidative water treatment. In this study, species-specific and/or apparent second order rate constants and mechanisms for the reactions of bromine and chlorine have been determined for various phenolic compounds (phenol, resorcinol, catechol, hydroquinone, phloroglucinol, bisphenol A, *p*-hydroxybenzoic acid, gallic acid, hesperetin and tannic acid) and flavone. The reactivity of bromine with phenolic compounds is very high, with apparent second order rate constants at pH 7 in the range of  $10^4$  to  $10^7 \text{ M}^{-1} \text{ s}^{-1}$ . The highest value was recorded for the reaction between HOBr and the fully deprotonated resorcinol ( $k = 2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). The reactivity of phenolic compounds is enhanced by the activating character of the phenolic substituents, e.g. further hydroxyl groups. With the data set from this study, the ratio between the species-specific rate constants for the reactions of chlorine versus bromine with phenolic compounds was confirmed to be about 3000.

Phenolic compounds react with bromine or chlorine either by oxidation (electron transfer, ET) or electrophilic aromatic substitution (EAS) processes. The dominant process mainly depends on the relative position of the hydroxyl substituents and the possibility of quinone formation. While phenol, *p*-hydroxybenzoic acid and bisphenol A undergo EAS, hydroquinone, catechol, gallic acid and tannic acid, with hydroxyl substituents in *ortho* or *para* positions, react with bromine by ET leading to quantitative formation of the corresponding quinones. Some compounds (e.g. phloroglucinol) show both partial oxidation and partial electrophilic aromatic substitution and the ratio observed for the pathways depends on the pH. For the reaction of six NOM extracts with bromine, electrophilic aromatic substitution accounted for only 20% of the reaction, and for one NOM extract (Pony Lake fulvic acid) it accounted for <10%. This shows that for natural organic matter samples, oxidation (ET) is far more important than bromine incorporation (EAS).

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## 1. Introduction

Chemical disinfection is widely used for the provision of safe drinking water. However, disinfection by-products (DBPs) are formed during disinfection processes from reactions between the applied chemical oxidants (e.g. chlorine) and naturally occurring organic and inorganic precursors, such as natural organic matter

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(NOM) and bromide (Sedlak and von Gunten, 2011; Heeb et al., 2014). Some DBPs pose potential health risks and are subject to regulation (Richardson et al., 2007; Hrudey, 2009; Hrudey and Charrois, 2012; Sedlak and von Gunten, 2011; Narotsky et al., 2013; Yang et al., 2014). Chlorination of bromide-containing water usually induces the formation of a mix of chlorinated and brominated DBPs (Richardson et al., 2003; Chowdhury et al., 2010; Hua and Reckhow, 2012; Pan and Zhang, 2013; Roccaro et al., 2014). During chlorination, bromide is oxidized to hypobromous acid/hypobromite ( $k_{\text{HOCl}/\text{Br}^-} = 1550 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_{\text{ClO}^-/\text{Br}^-} = 9 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ ; Kumar and Margerum, 1987), which are the main bromine species formed in fresh waters (Heeb et al., 2014).

Phenolic groups are known constituents of NOM and phenolic compounds (the term phenols is also used in the text to represent polyhydroxy aromatic compounds) have often been used as model compounds to represent substructures within NOM (Bond et al., 2009). Hypohalous acids (chlorine, bromine, iodine) can react with phenols through electrophilic aromatic substitution (EAS), as well as by oxidation, *i.e.*, electron transfer (ET) reactions (Rook, 1976, 1977; Gallard and von Gunten, 2002).

HOBr is generally more reactive than HOCl. For phenolic compounds, QSAR modelling showed a ratio of the second order rate constants for the reactions of HOBr or HOCl with phenolic compounds,  $k_{\text{HOBr}}/k_{\text{HOCl}}$  of  $\approx 3 \times 10^3$ , demonstrating the high propensity of phenolic compounds to bromination as compared to chlorination if bromide is present in the water (Heeb et al., 2014). The rate for the reactions of chlorine and bromine with phenolic compounds is pH-dependent due to the differences in reactivity of the hypohalous acid and the hypohalite anion and the higher reactivity of the phenolate compared to the phenol (Rebenne et al., 1996; Gallard and von Gunten, 2002; Deborde and von Gunten, 2008; Heeb et al., 2014). This can be explained by the higher electrophilicity of HOX compared to  $\text{XO}^-$  and the increased electron density of the phenolate compared to the phenol (Heeb et al., 2014). Based on this reactivity pattern, apparent second order rate constants are pH dependent and show a maximum at the mean of the pKa values of the two involved acid-base couples ( $\text{HOX}/\text{OX}^-$  and phenol/phenolate) (Heeb et al., 2014; Criquet et al., 2012).

Phenol groups are strongly activating and direct EAS reaction in *ortho*- or *para*-positions. The products of EAS reactions of phenols with HOX are mono-, di- and tri-halophenols. These reactions have been studied in some detail because of the off-flavour characteristics of the products and their role for taste and odour of drinking waters (Gallard et al., 2003; Acero et al., 2005; Heitz et al., 2003). For some phenols, particularly those with two hydroxy groups in *meta* position to each other, the reaction pathway includes ring-opening of the aromatic ring and production of regulated DBPs such as the trihalomethanes (THMs) (Boyce and Hornig, 1983). The formation of THMs from a variety of phenolic compounds has been extensively studied (Ichihashi et al., 1999; Chang et al., 2006; Arnold et al., 2008). However, depending on the substitution patterns on the aromatic ring, the yield of THM formation can be vastly variable. Among phenols, resorcinol (1,3-dihydroxybenzene) showed the highest yield of THM formation (Norwood et al., 1980; Bichsel and von Gunten, 2000). In contrast, Bond et al. (2009) demonstrated that despite a high chlorine demand, tannic acid (a polymer of gallic acid (3,4,5-trihydroxybenzoic acid); for structure, see Supporting Information (SI), Fig. S1) showed a low DBP substitution efficiency (0.5% of Cl-incorporation compared to *ca.* 45% for resorcinol). It was proposed that chlorine was consumed in oxidation of tannic acid and/or in production of other DBPs, which weren't measured (Bond et al., 2009). Oxidation of phenolic compounds can potentially lead to quinone type structures (Wenk et al., 2013). These electron transfer (ET) reactions depend strongly on the electronic properties of the substituents and electron-withdrawing

substituents can inhibit this reaction completely. Moreover, halobenzoquinones have been identified as chlorine/bromine disinfection by-products in drinking water (Zhao et al., 2012; Wang et al., 2014). Haloquinones were previously predicted as potential DBPs (Bull et al., 2006) and they may be relevant to the known elevated risk of human bladder cancer due to consumption of chlorinated drinking water (Mills et al., 1998).

In the current study, apparent and species-specific second order rate constants for the reactions of bromine and chlorine with a variety of phenolic compounds were determined. Furthermore, the extent of the reaction of bromine with phenolic compounds and NOM extracts by electrophilic aromatic substitution and/or oxidation processes was investigated.

## 2. Materials and methods

### 2.1. Chemicals

All reagents used were of the highest available purity. Bromine solutions were produced from a chlorine stock solution and bromide as described previously (Criquet et al., 2012). Briefly, an aliquot of a chlorine stock solution (1.2 M) is added to a solution of bromide with a slight excess of bromide compared to chlorine concentration (5%). Experiments were performed in ultrapure water (Barnstead Nanopure (Skan); TOC <0.2 mg L<sup>-1</sup>; 18.2 mΩ cm). The pH was controlled by 5 mM phosphate, borate, or carbonate buffers. Poorly soluble compounds were solubilized in methanol; the effect of methanol (usually <0.5% v/v, except for the determination of the reactivity of chlorine with flavone, where MeOH was present at <5% v/v) in our experimental systems was tested and found not to interfere with the experiments related to kinetics or elucidation of reaction pathways. The structures of the phenolic compounds used for the kinetic studies are presented in Table 1. The NOM extracts were purchased from the International Humic Substances Society (IHSS); the percentage of aromatic carbon has been reported previously (Thorn et al., 1989). Suwannee River DOM (SRDOM; catalogue number: 2R101N; aromatic carbon: 23%), Suwannee River humic acid (SRHA; catalogue number: 2S101H; aromatic carbon: 31%), Suwannee River fulvic acid (SRFA; catalogue number: 2S101F; aromatic carbon: 22%), Nordic reservoir NOM (NR; 1R108N; aromatic carbon: 19%), Pony Lake fulvic acid (PL; 1R109F; aromatic carbon: 12%), Elliot soil humic acid (ESHA; catalogue number: 1S102H; aromatic carbon: 50%) and Leonardite humic acid (LEHA; catalogue number: 1S104H; aromatic carbon: 58%) were used as received. We chose to use commercially available DOM extracts because they have been used as references in oxidation studies, and their chemical properties are known. Furthermore, these extracts represent a wide variety of organic materials from allochthonous (SR and NR) and autochthonous (PL) aquatic systems to extracts from agricultural soil (ES) and lignite coal mining (LE).

### 2.2. Analytical methods

Bromide analyses were performed by ion chromatography (Dionex ICS 3000) on an AS9-HC column with a quantification limit of 10 µg L<sup>-1</sup> and a standard deviation of ±10% (Salhi and von Gunten, 1999). The oxidant concentration was measured using the colorimetric method based on diethyl-*p*-phenylene diamine (DPD) by an absorbance measurement of the sample at 515 nm (Rodier et al., 2009). A linear calibration was performed with oxidant concentrations in the range of 0.1–5 µM with a 5 cm cell for better accuracy at low concentrations. When needed, the gallic acid concentration was analyzed by high performance liquid chromatography (HPLC) (Agilent 1100) with a 15 cm long, 0.4 cm i.d.

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