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Transformation of aminopyrine in the presence of free available chlorine: Kinetics, products, and reaction pathways

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HIGHLIGHTS

- Aminopyrine (AMP) chlorination included the reactions of AMP with HOCl, Cl_2, and Cl_2O.
- The reactivity of each FAC species toward AMP: HOCl < Cl_2 < Cl_2O.
- The contribution of each FAC species at neutral pH (no Cl^- added): HOCl > Cl_2O > Cl_2.
- The role Cl_2 became significant in the presence of Cl^- at acidic pH.
- AMP underwent pyrazole ring opening, hydroxylation, dehydrogenation, and halogenation.

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ABSTRACT

Aminopyrine (AMP) has been frequently detected in the aquatic environment. In this study, the transformation mechanism of AMP by free available chlorine (FAC) oxidation was investigated. The results showed that FAC reacted with AMP rapidly, and a 74% elimination was achieved for 1.30 μM AMP after 2 min at 14.08 μM FAC dose. AMP chlorination was strongly pH-dependent, and its reaction included second- and third-order kinetic processes. Three active FAC species, including chlorine monoxide (Cl_2O), molecular chlorine (Cl_2), and hypochlorous acid (HOCl), were observed to contribute to AMP degradation. The intrinsic rate constants of each FAC species with neutral (AMP^0) and cation (AMP^+) species were obtained by kinetic fitting. Cl_2O exhibited the highest reactivity with AMP^0 ($k_{AMP^0, Cl2O} = (4.33 \pm 1.4) \times 10^9\ M^{-1}s^{-1}$). In addition, Cl_2 showed high reactivity (10^6–$10^7\ M^{-1}s^{-1}$) in the presence of chloride, compared with HOCl ($k_{AMP^+, HOCl} = (5.73 \pm 0.23) \times 10^2\ M^{-1}s^{-1}$, $k_{AMP^0, HOCl} = (9.68 \pm 0.96) \times 10^2\ M^{-1}s^{-1}$). At pH 6.15 and 14.08 μM FAC dose without chloride addition, the contribution of Cl_2O reached to the maximum (33.3%), but in the whole pH range, HOCl was the main contributor (>66.6%) for AMP degradation. The significance of Cl_2 was noticeable in water containing chloride. Moreover, 11 transformation products were identified, and the main transformation pathways included pyrazole ring breakage, hydroxylation, dehydrogenation, and halogenation.

1. Introduction

The occurrence of pharmaceuticals and personal care products (PPCPs) has been repeatedly observed in wastewater, surface water, and even in drinking water around the world and has attracted a widespread attention because Richardson and Bowron first confirmed that PPCPs were present at trace level (μg L^{-1}–ng L^{-1}) in the effluents of wastewater treatment plants (WWTPs) (Mompelat et al., 2009; Richardson and Bowron, 1985). The continuous increase in PPCP production and usage, the characteristics of persistence and nonbiodegradability, and the incomplete removal of these pollutants have permitted their spread in natural waters. Because of the widely varying types and physicochemical properties of these compounds, conventional drinking water treatment technologies (i.e., coagulation-sedimentation-filtration) usually cannot remove all PPCPs effectively. Therefore, it is unavoidable that certain PPCPs can reach tap water after escaping from conventional drinking water treatment processes, which poses a threat to human health due to their potential ecotoxicity (Cleuvers, 2003;

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Crane et al., 2006; Jones et al., 2003).

In conventional water treatment plants, the disinfection process has played a relatively significant role in the removal of certain PPCPs, compared with coagulation-sedimentation-filtration (Kim et al., 2007; Kosma et al., 2010; Simazaki et al., 2008; Vieno et al., 2007; Westerhoff, 2003). As a low-cost disinfectant, free available chlorine (FAC) is globally the most used chemical oxidant for drinking water and wastewater disinfection (Gibs et al., 2007; Glassmeyer and Shoemaker, 2005; Lee and von Gunten, 2010; Rodil et al., 2012; Sharma, 2008). Prior studies discovered that FAC can react with some PPCPs selectively and effectively, including acetaminophen, naproxen, diclofenac, antipyrine, sulfamethoxazole, and 17β-estradiol (Acero et al., 2010; Cai et al., 2013a, 2013b; Dębska et al., 2004; Dodd and Huang, 2004; Rodil et al., 2012; Soufan et al., 2012; Xagoraraki et al., 2008). Many FAC active species exist during chlorination, such as hypochlorous acid (HOCl), hypochlorite (OCl^-), chlorine monoxide (Cl_2O), and molecular chlorine (Cl_2) (Reactions 1 and 2) (Beach and Margerum, 1990; Cherney et al., 2006; Deborde and von Gunten, 2008; Sivey et al., 2010; Sivey and Roberts, 2012). Usually, Cl_2 and Cl_2O can be neglected under typical water disinfection conditions because of their very low concentrations (Deborde and von Gunten, 2008). However, despite the relatively lower concentrations of Cl_2 and Cl_2O, they may possess much higher reactivities than HOCl for removing some pharmaceuticals (Cherney et al., 2006; Chusaksri et al., 2012; Sivey et al., 2010; Sivey and Roberts, 2012). Compared to other oxidation processes (e.g., ClO_2, O_3, UV), FAC is a weaker oxidant and has less reactivity; because of these properties, FAC is usually unable to degrade these micropollutants completely. Instead, FAC converts them into daughter products by chlorine substitution reaction or oxidation (Bedner and MacCrehan, 2006; Boyd et al., 2005; Dodd and Huang, 2007, 2004; Dodd et al., 2005; Li et al., 2011; Shah et al., 2006), which show higher biotoxicity than parent compounds such as acetaminophen and naproxen (Bedner and MacCrehan, 2006; Boyd et al., 2005).

$$2HOCl \overset{k_1}{\leftrightarrow} Cl_2O + H_2O$$
$$k_1 = 8.74 \times 10^{-3}\ M^{-1}\ (25\ ^\circ C)(\text{Sivey et al. 2010}) \quad (1)$$

$$HOCl + Cl^- + H^+ \overset{k_2}{\leftrightarrow} Cl_2 + H_2O$$
$$k_2 = 2.3 \times 10^3\ M^{-2}\ (25\ ^\circ C)\ (\text{Beach and Margerum 1990}) \quad (2)$$

Aminopyrine (AMP) is a pyrazolone compound (for the structure of AMP, see Fig. S1 in Supplementary Materials and Table 3) and has been used as an analgesic, antipyretic, and anti-inflammatory drug since the end of the 1990s (Costa et al., 2006). It can lead to granulocytopenia (i.e., an abnormal decrease in the total number of granular leukocytes in the blood), the formation of nitrosamine carcinogens, and myelosuppression (i.e., a reduction in the ability of the bone marrow to produce blood cells). Previous studies have found AMP in the WWTPs (Jelicic and Ahel, 2003; Koutsouba et al., 2003; Zuehlke et al., 2004), drinking water treatment plants (DWTPs) (Reddersen et al., 2002; Zuhlke et al., 2004), and ground water (Reddersen et al., 2002; Zuehlke et al., 2004, 2007; Zuhlke et al., 2004) in Germany and Greece at concentrations up to 0.4 μg L^{-1}. Relatively low removal rates of AMP (38%) have been observed in WWTPs (Jelicic and Ahel, 2003; Ternes, 1998), indicating that a significant fraction of it may enter the receiving natural waters and subsequently threaten human health. Previous reports observed that pyrazolone compounds can be transformed rapidly by FAC in several seconds (Cai et al., 2014, 2013a, 2013b; Rodil et al., 2012). Some strong oxidants (e.g., ClO_2, O_3, and Fe (VI)) also exhibited the appreciable removal efficiencies toward AMP (Huber et al., 2005; Lee et al. 2007, 2008; Miao et al., 2015). Under the existence of singlet oxygen (Duchstein et al., 1988; Weber and Wollenberg, 1988), sodium periodate (Weber and Wollenberg, 1988) and hydrogen peroxide (Weber and Bresser, 1996), or in the condition of photochemical oxidation (Marciniec, 1985a, 1985b), AMP could be degraded or decomposed to form 1-acetyl-1-methyl-2-dimethyloxamoyl-2-phenylhydrazide (AMDOPH) and 1-acetyl-1-methyl-2-phenylhydrazide (AMPH), suggesting that AMP is typically not easy to be mineralized by oxidation. To our knowledge, there is limited information available on the fate and transformation mechanism of AMP during conventional DWTPs (Cai et al., 2014).

Given that the disinfection treatment is the last barrier of PPCPs reaching to drinking water during DWTPs, it is necessary to explore the reaction kinetics and transformation products of AMP during the disinfection with FAC. Therefore, the aims of this study were (1) to determine the reaction order of AMP chlorination and elucidate the kinetics of AMP chlorination; (2) to investigate the influence of chloride, pH, and variable solution conditions (ionic strength and buffer solutions) on AMP chlorination; and (3) to identify transformation products of AMP chlorination and propose the possible transformation pathways during AMP chlorination.

2. Materials and methods

2.1. Chemicals and reagents

Sources of chemicals and reagents are provided in Supplementary Materials Text S1.

2.2. Analytical methods

The analytical methods used in this study are shown in Text S2.

2.3. Kinetic experiments of AMP chlorination in ultrapure water

An AMP solution (10 mg L^{-1}, ≈43 μM) was prepared by diluting a stock solution (2.5 mM AMP) with ultrapure water. Amber borosilicate bottles with glass stoppers (30 mL) were used as reactors, and the reaction volume was controlled at 25 mL. All experiments were performed under the condition of FAC dose excess ($[FAC]_0/[AMP]_0 > 10$) with continuous magnetic stirring. The reaction temperature was controlled at 25 ± 1 °C by placing the reactor into a beaker of water, which was on a magnetic-heated stirrer (RCT basic, IKA, Germany). Kinetic experiments were initiated by spiking FAC stock solution (≈1.4 mM) into the reactors containing AMP. Each sample (1 mL) was obtained at regular time intervals and immediately quenched with 10 μL sodium thiosulfate (31.64 mM). Supplementary experiments were conducted at different pH to confirm that sodium thiosulfate exhibited a negligible effect on the AMP degradation in the oxidant-free controls and the experiments dosed with FAC (Text S3). The residual concentration of AMP was analyzed by Rapid Resolution Liquid Chromatography system (RRLC 1260, Agilent, USA) equipped with a variable wavelength UV detector after filtering through a 0.45-μm glass–fiber filter (for detailed analytical method, see Text S2). All experiments were conducted in duplicate or triplicate, and the averaged data are presented.

Buffer solutions of 10 or 1 mM acetate (pH 3.00–5.00), phosphate (pH 5.50–8.00), and borate (pH 8.50–9.00) were used to control the solution pH. NaOH and HNO_3 were used to adjust the final desired pH values. The solution pH did not vary by more than 0.2 unit at the initial and final point of each experiment. The concentration of methanol during each experiment was below 0.02%