Photodegradation of haloacetonitriles in water by vacuum ultraviolet irradiation: Mechanisms and intermediate formation

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ABSTRACT

Photodegradation of haloacetonitriles (HANs), highly carcinogenic nitrogenous disinfection by-products, in water using vacuum ultraviolet (VUV, 185 + 254 nm) in comparison with ultraviolet (UV, only 254 nm) was investigated. Monochloroacetonitrile (MCAN), dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), and dibromoacetonitrile (DBAN) were species of HANs studied. The effect of gas purging and intermediate formation under VUV were examined. The results show that the pseudo first order rate constants for the reduction of HANs under VUV were approximately 2−7 times better than UV. The order of degradation efficiency under VUV and UV was MCAN < DCAN < TCAN < DBAN. The degradation efficiencies of individual HANs under VUV were higher than those of mixed HANs, suggesting competitive effects among HANs. Under nitrogen purging, the removal rate constants of mixed HANs was much higher than that of the aerated condition by 34.4, 34.9, 10.1, and 3.8 times for MCAN, DCAN, TCAN, and DBAN, respectively. The major degradation mechanism for HANs was different depending on HANs species. Degradation intermediates of HANs such as 2-chloropropionitrile, 2,2-dimethylpropanenitrile, and fumaronitrile were produced from the substitution, addition, and polymerization reactions. In addition, chlorinated HANs with lower number of chlorine atom including MCAN and DCAN were found as intermediates of DCAN and TCAN degradation, respectively.

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1. Introduction

During the last decade, emerging unregulated nitrogenous disinfection by-products (N-DBPs), such as haloacetonitriles (HANs), halonitromethanes (HNMs), haloacetamides (HAcAms), and nitrosamines, have gained attentions than regulated carbonaceous DBPs (C-DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs). This is because N-DBPs have higher toxicity than C-DBPs (Muellner et al., 2007). The first three groups of N-DBPs were surveyed at 12 drinking water treatment plants in the United States and HANs were the group with the highest concentration (Krasner et al., 2006). As high as 14 μg L^{-1} was observed for total HANs (THAN), including dichloroacetonitrile (DCAN), dibromoacetonitrile (DBAN), bromochloroacetonitrile (BCAN), and trichloroacetonitrile (TCAN). The most prevalent species among HANs detected was DCAN, which accounted for >90% of THAN detected (Krasner et al., 2006; Baytak et al., 2008). HANs level in treated water could be from few microgram per liter to almost a hundred microgram per liter (Baytak et al., 2008; Guilherme and Rodriguez, 2014). A relatively high THAN concentration of 88.4 μg L^{-1} was observed in tap water of Izmir, Turkey (Baytak et al., 2008). Based on studies in the United States (Krasner et al., 2006) and Canada (Guilherme and Rodriguez, 2014), the concentration of THAN was >10 times less than those of THMs and HAAs. The cytotoxicity of HANs is nearly 200 times higher than that of regulated HAAs (Muellner et al., 2007). Due to their adverse health effects, the

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World Health Organization (WHO) suggests a guideline value of 70 μg L^{-1} for DBAN, and a provisional guideline value of 20 μg L^{-1} for DCAN (WHO, 2011). These guidelines have not been adopted and there is no standard for HANs in any countries. HANs have been included in the U.S. EPA Information Collection Rules and will potentially be regulated in the future.

The formation of HANs is tied to the reaction between chlorine or chloramine and dissolved organic nitrogen (DON) in water (Lee et al., 2007). Hydrophilic fraction (accounts for >80% of DON) was the main precursor of HANs formation (Huo et al., 2013). To control the concentration of HANs in water, there are two approaches including removal of HANs precursors and removal of HANs directly (after they are formed). However, the removal of precursors by conventional water treatment processes of coagulation, sedimentation, and filtration may be difficult since they are mostly hydrophilic (Westerhoff and Mash, 2002). Therefore, post-treatment or point of use treatment for HANs removal is needed. Various methods to treat N-DBPs have been studied such as biological treatment (Webster et al., 2013), reduction by zero-valent zinc (Han et al., 2013), and adsorption by silica materials (Prarat et al., 2011). Although these methods can reduce N-DBPs concentration, but it is costly, time consuming, and generating waste. Recently, advanced oxidation processes (AOPs) have been reported to be effective for the removal of N-DBPs in water. Examples of such AOPs used to treat HANs include solar photolysis (Chen et al., 2010), sonolytic ozonation (Park et al., 2012), and photocatalysis ozonation (Shin et al., 2013). Complete removal of DCAN was reported under photocatalysis ozonation with less energy consumption (high energy efficiency) (Shin et al., 2013). Nevertheless, most of AOPs require additional chemical/catalyst to generate hydroxyl radical (OH•). Vacuum ultraviolet (VUV) is an alternative treatment of AOPs that generate OH• in situ by water homolysis. VUV emits light at the wavelength (λ) lower than 200 nm causing water molecules to break into hydrogen atom (H•) and OH•, as shown in Equation (1) (Zoschke et al., 2014). Therefore, contaminants could be degraded through direct photolysis or by oxidation with OH• (indirect photolysis).

$$H_2O + h\nu(\lambda < 190nm) \rightarrow H^{•} + OH^{•} \qquad (1)$$

Low pressure mercury (LP-Hg) lamp is one of VUV light sources. The lamp emits polychromatic light at 185 nm (10%) and 254 nm (90%) (Oppenländer, 2003). The advantages of LP-Hg VUV (hereafter referred to as VUV) is that it can generate OH• without additional of chemicals and therefore reduces the operation cost. Also, its setup and installation are simple and can be retrofitted to an existing UV disinfection chamber. During the past decade, a number of previous studies have demonstrated that VUV are effective for degradation of many contaminants such as pharmaceutical compounds (Szabó et al., 2011), taste and odor compounds (Kutschera et al., 2009), and natural organic matter (NOM) (Ratpukdi et al., 2010). Therefore, VUV could be a promising technology for post treatment of N-DBPs including HANs. UV photolysis for the removal of HANs (Chen et al., 2010), HNMs (Fang et al., 2013), and iodinated THMs (Xiao et al., 2014) have been studied. Some of DBPs could be removed by UV photolysis at the same dose for UV disinfection at neutral or alkaline pH. Their removal rate constants depend upon the type and number of halogen atoms. However, no information is available on the application of VUV for the removal of HANs.

The main objective of this research was to investigate photodegradation of four model compounds of HANs (MCAN, DCAN, TCAN, and DBAN) by VUV in comparison with conventional UV which is typically used for disinfection. The removal efficiency and the kinetic rate constants of single and mixed-HANs were compared. The effect of gas purging was studied. The degradation mechanism of HANs by direct and indirect photolysis was elucidated. In addition, the intermediate products from VUV treatment were examined.

2. Material and methods

2.1. Water samples

Four HANs species; MCAN (98%, Wako, Japan), DCAN (98%, Sigma-Aldrich, USA), TCAN (98%, Sigma-Aldrich, USA), and DBAN (90%, Acros Organics, USA), were chosen according to the occurrence data and toxicity (Krasner et al., 2006; Muellner et al., 2007). Water samples were prepared as single and mixed HAN solutions by dissolving the compound(s) in acetone and subsequently diluting with de-ionized water. The concentration of acetone in the reaction (after the dilution) was 0.136 mM. This concentration of acetone (<4 mM) does not affect the degradation of organic compounds (Li and Goel, 2010). The rate constant for the reaction of OH• with acetone is $1.1 \times 10^8 \, M^{-1} \, s^{-1}$ which is much lower than that for the reaction of OH• with HANs in this study (1.35–$2.80 \times 10^9 \, M^{-1} \, s^{-1}$). Moreover, acetone has very low molar absorptivity under UV, 254 nm ($13.9 \, M^{-1} \, cm^{-1}$) (Feigenbrugel et al., 2005). Therefore, the competitive effect of the solvent during indirect and direct photolysis can be neglected. The degradation of HANs under VUV and UV was carried out at an initial concentration of 100 μg L^{-1} for each compound. For intermediate identification, only VUV treatment was examined at high initial concentrations of HANs (100 and 500 mg L^{-1}). To maintain pH around 7 throughout the reaction, the samples were prepared in a phosphate buffer solution (ionic strength at 10 mM) (Prarat et al., 2011). The buffer solution was prepared from disodium hydrogen phosphate heptahydrate (Na$_2$HPO$_4$·7H$_2$O, Panreac, Spain) and sodium dihydrogen phosphate monohydrate (NaH$_2$PO$_4$·H$_2$O, Carlo Erba, France).

To study the degradation mechanism by direct and indirect photolysis, methylene blue (MB, Merck, Germany) as a probe compound for OH• was prepared in deionized water, and spiked into the HANs solutions at a concentration of 10 μM. (Keen et al., 2012). Tert-butanol (TBA, 99%, Fluka, Germany), as a scavenger for OH•, was also added into the HANs solutions at 20 mM prior to VUV irradiation (Liao et al., 2013). The photon flux and an effective optical path length were determined by the degradation of H$_2$O$_2$ (>30% w/v, Fisher, UK) in water (Xiao et al., 2015).

2.2. Experimental setup

Photodegradation experiments (Supplementary Material, Fig. S1) were performed in a tubular borosilicate reactor (15 cm×45 cm). LP-Hg-VUV lamps (185 + 254 nm, model GPH383T5/VH/HO, Universal Lights Source, Inc., San Francisco, CA, USA) were used as a light source for VUV. LP-Hg-UV lamps (only 254 nm, model GPH383T5/L/HO) were used for UV experiments. Two lamps were installed in the reactor providing a total power input of 60 W (30 W/lamp). The photon flux for UV, 254 nm determined by H$_2$O$_2$ actinometry was 1.8×10^{-6} E L^{-1} s^{-1}. For low pressure (LP)-VUV lamp, the photon flux of UV, 185 nm was 10% of that of UV, 254 nm radiation (Oppenländer, 2003), which was 1.8×10^{-7} E L^{-1} s^{-1}. These photon fluxes are equivalent to the intensities for UV (254 nm) and VUV (185 + 254 nm) systems of 5.84 and 6.64 mW cm^{-2} (5.84 + 0.80 mW cm^{-2}), respectively.

2.3. Experimental procedure

All experiments were operated in a batch mode using 6 L of the