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UV-Induced Transformation of Four Halobenzoquinones in Drinking Water

Yichao Qian,[#] Wei Wang,[#] Jessica M. Boyd, Minghuo Wu, Steve E. Hrudey, and Xing-Fang Li*

Division of Analytical and Environmental Toxicology, Department of Laboratory Medicine and Pathology, University of Alberta, Edmonton, Alberta, Canada, T6G 2G3

Ⓢ *Supporting Information*

ABSTRACT: Halobenzoquinones (HBQs) are a group of emerging disinfection byproducts (DBPs) found in treated drinking water. Because the use of UV treatment for disinfection is becoming more widespread, it is important to understand how the HBQs may be removed or changed due to UV irradiation. Water samples containing four HBQs, 2,6-dichloro-1,4-benzoquinone (DCBQ), 2,3,6-trichloro-1,4-benzoquinone (TCBQ), 2,6-dichloro-3-methyl-1,4-benzoquinone (DCMBQ), and 2,6-dichloro-1,4-benzoquinone (DBBQ), were treated using a modified bench scale collimated beam device, mimicking UV treatment. Water samples before and after UV irradiation were analyzed for the parent compounds and products using a high performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) method. As much as 90% of HBQs (0.25 nmol L^{-1}) in both pure water and tap water were transformed to other products after UV_{254} irradiation at 1000 mJ cm^{-2}. The major products of the four HBQs were identified as 3-hydroxyl-2,6-dichloro-1,4-benzoquinone (OH-DCBQ) from DCBQ, 5-hydroxyl-2,6-dichloro-3-methyl-1,4-benzoquinone (OH-DCMBQ) from DCMBQ, 5-hydroxyl-2,3,6-trichloro-1,4-benzoquinone (OH-TCBQ) from TCBQ, and 3-hydroxyl-2,6-dibromo-1,4-benzoquinone (OH-DBBQ) from DBBQ. These four OH-HBQs were further modified to monohalogenated benzoquinones when the UV dose was higher than 200 mJ cm^{-2}. These results suggested possible pathways of UV-induced transformation of HBQs to other compounds. Under the UV dose commonly used in water treatment plants, it is likely that HBQs are partially converted to other halo-DBPs. The occurrence and toxicity of these mixed DBPs warrant further investigation to understand whether they pose a health risk.
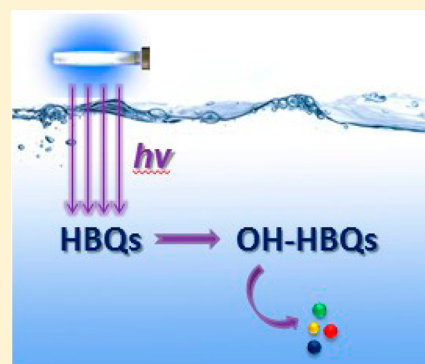
1. INTRODUCTION

Disinfection is an essential process for assuring safe drinking water.[1] However, an increasing number of disinfection byproducts (DBPs) have been identified as unintentional products of chlorine disinfection.[2] DBPs have received considerable attention for possible adverse human health consequences from long-term consumption of chlorinated drinking water with the most consistent and plausible concern being an increased risk of bladder cancer.[3] However, as yet, no class of DBPs has been identified with both the carcinogenic potency and the prevalence in drinking water to explain the observed epidemiologic estimates for bladder cancer risk.

Halobenzoquinones (HBQs) have recently been confirmed as a group of emerging DBPs that may be relevant to bladder cancer risk.[4,5] A study of nine water treatment plants (WTPs) in Canada and the United States found 2,6-dichloro-1,4-benzoquinone (DCBQ) to be the most abundant HBQ (up to 275 ng/L) as well as to occur most frequently (9/9 plants).[6] Three other HBQs, 2,6-dichloro-3-methyl-1,4-benzoquinone (DCMBQ), 2,6-dibromo-1,4-benzoquinone (DBBQ), and 2,3,6-trichloro-1,4-benzoquinone (TCBQ), were also detected at low ng/L concentrations in disinfected drinking water. Quantitative structure toxicity relationship (QSTR) analysis has predicted that some HBQs may be toxicologically relevant [5]

and may have potential genotoxicity as observed from their interaction with genetic material and in vitro toxicity testing.[7,8] However, the fate and transformation of HBQs during the treatment processes and within the distribution system is not clear.

Ultraviolet (UV) irradiation has emerged as an effective alternative disinfection technology. An online survey in the United States showed that at least 27 WTPs in the lower 48 states have introduced UV disinfection into their water treatment process, and more applications are under consideration due to the recently promulgated regulations by the US Environment Protection Agency.[9] UV disinfection is desirable because of its well-known ability to inactivate chlorine-resistant microorganisms (e.g., *Cryptosporidium* and *Giardia*) [10] and due to the lack of chemical inputs; UV disinfection was originally believed to limit the formation of regulated DBPs in water.[11] However, UV irradiation can change the chemical composition in the water body, and the photolysis products of natural organic matter (NOM) and small organic/inorganic com-
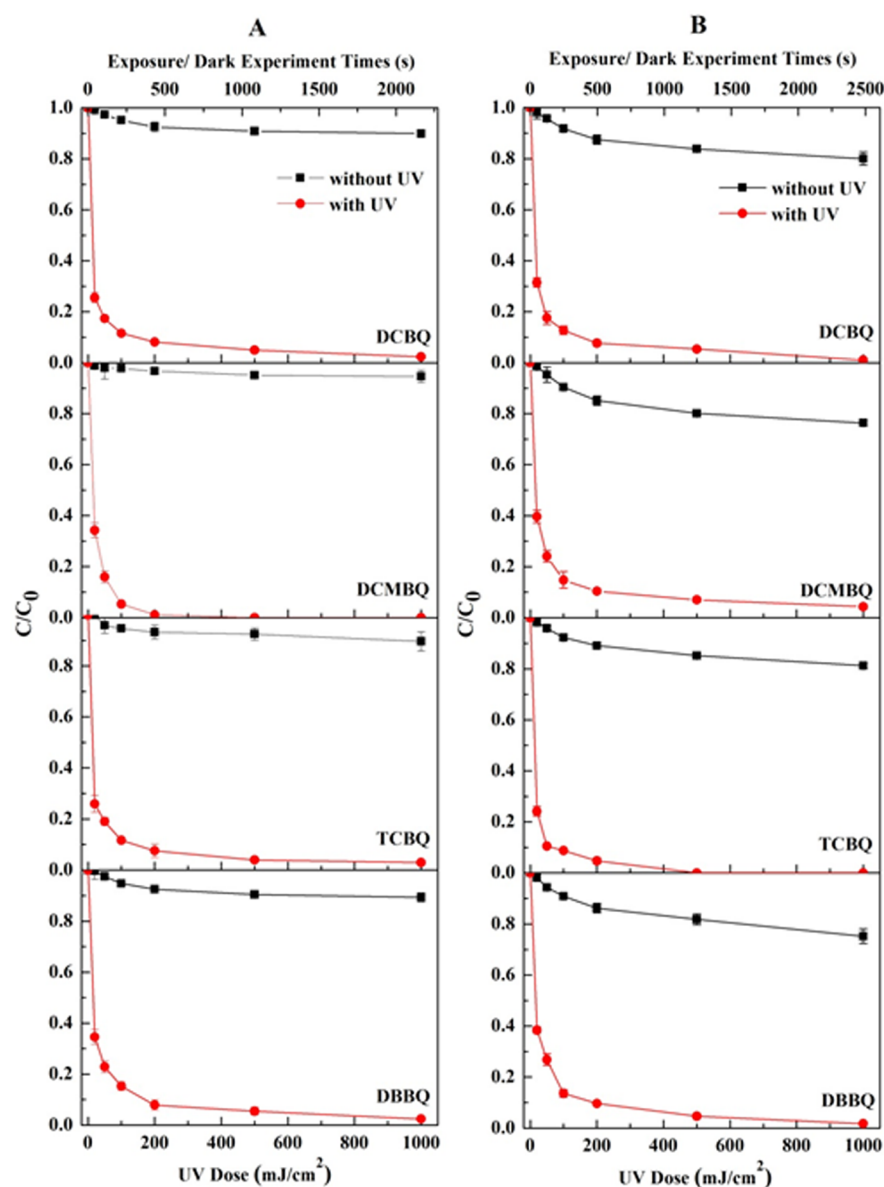
Figure 1. Photodecay of four halobenzoquinones in Optima water (left, A) and tap water (right, B) by UV_{254} over the experimental period. The second horizontal axis indicates the exposure/dark experiment times.

pounds were demonstrated to be the precursors of DBPs when coupled with chemical disinfection.[12,13] Several studies have reported the enhanced formation of some regulated DBPs due to the generation of precursors resulting from the photolysis-chlorination reactions.[13−15] Organic precursors and DBPs themselves in water can be the possible UV degradation targets. Li et al.[16] have reported that monochloroacetic acid (MCAA), a halogenated organic compound (HOC), could be degraded rapidly in the sulfite/UV process, while inorganic chloramine was degraded into nitrite, nitrate, nitrous oxide, and ammonium by UV_{254} irradiation.[17] N-Nitrosodimethylamine (NDMA), the most prevalent nitrogenous DBP, can be effectively degraded by UV treatment in drinking water.[18−20] However, information on UV-induced transformations of HBQs in the drinking water system is not available. Therefore, this study aims to examine the fate of HBQs during UV irradiation.

In the present study, we have focused on the four halobenzoquinones, DCBQ, DCMBQ, TCBQ, and DBBQ,

that have been detected in drinking water. Water samples containing these HBQs were irradiated by UV_{254}, and the degradation of these compounds was investigated. The photodegradation products were identified using a high resolution triple quadrupole time-of-flight (TOF) mass spectrometer. On the basis of the identification of the major products, we proposed potential photodecay processes of these HBQs. This is the first set of results to show the fate of HBQs and the formation of other HBQ-related DBPs in water when UV irradiation is used.

2. MATERIALS AND METHODS

2.1. Reagents and Chemicals. DCBQ was purchased from Sigma-Aldrich (St. Louis, MO); DBBQ was purchased from Indofine Chemical Company (Hillsborough, NJ), and DCMBQ and TCBQ were synthesized by Shanghai Acana Pharmtech (Shanghai, China). The water and methanol used in this study were Optima LC/MS grade purchased from Fisher

Scientific (Fair Lawn, NJ). LC/MS grade formic acid (FA, 49−51%) was obtained from Sigma-Aldrich (St. Louis, MO).

2.2. UV Systems. A bench scale collimated beam device was employed to conduct UV experiments (Figure S1, Supporting Information). The lamp system consisted of two 8W UVC germicidal lamps (Luzchem LZC-UVC-01), with a strong line at 254 nm. The UV light passed through a 11.5 cm diameter aperture into a 400 mL water sample in an uncovered cylindrical crystallization dish (11.5 cm diameter × 7.6 cm depth). The distance from the lamp to the water surface was 15.2 cm, and the water sample depth was 3.8 cm. The UV irradiance at the surface of water was measured by the UVX model digital radiometer (UVP). During the irradiation, the water sample was stirred continuously. Several corrections were performed, and the average UV irradiance was calculated according to the standardized method reported by Bolton and Linden.[21] The details of the corrections are described in the Supporting Information. The UV dose (mJ cm^{-2}) was calculated as the product of UV irradiance (mW cm^{-2}) multiplied by the exposure time (s). In this study, the target UV doses were set at 20, 50, 100, 200, 500, and 1000 mJ cm^{-2} and the exposure periods were determined in advance depending on the compounds tested.

2.3. Water Samples. Four HBQ standard stock solutions were prepared by dissolving HBQs into Optima methanol to a concentration of each HBQ of 1000 μg mL^{-1}. These stock solutions were freshly prepared monthly and kept at −20 °C. A preliminary set of experiments using high levels of HBQs were conducted to compare the removal efficiency in pure solution (containing one HBQ standard) and mixed solution (containing four HBQ standards). Water samples were prepared by spiking specific HBQs into 400 mL of Optima water and tap water. The physical characteristics of tap water and Optima water are presented in Table S2, Supporting Information. The results from the preliminary experiments showed that the transformation efficiencies of four HBQs were similar when they were present in solutions alone compared with those in a mixture (Figures S2 and S3, Supporting Information). Therefore, we used individual HBQs (0.25 nmol L^{-1}) in Optima water and tap water to further investigate the photodecay of four HBQs. This testing concentration is in the range of the actual concentration of HBQs that has been detected in drinking water.

In separate sets of experiments to identify the transformation products, the initial concentration of each HBQ was 0.5 μmol L^{-1} so that the solution could be analyzed directly without preconcentration, thereby avoiding the variation caused by the pretreatment. Precleaned amber glass bottles with PTFE screw caps were used to store the samples. The pH of solution (adjusted with 0.1 M sodium hydroxide) was 7.5 ± 0.1.

2.4. Experimental Procedures. To obtain photodecay curves, water samples (400 mL each) containing 0.25 nmol L^{-1} of individual HBQs in the Optima water and tap water were freshly prepared immediately prior to UV irradiation. At each time point, one sample was irradiated by UV$_{254}$ and another was kept in the dark. After being irradiated for a given time, the two samples were acidified with 2 mL of FA and analyzed for the HBQs using a high performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) method with multiple reaction monitoring (MRM) mode. Each data point in Figure 1 was the average of duplicate experiments.

To identify the UV-induced transformation products, the water samples containing 0.5 μmol L^{-1} of each individual HBQ

were prepared. In parallel, one of the same samples (400 mL) was kept in the dark while another sample (400 mL) was irradiated using UV$_{254}$. At a given time after irradiation, an aliquot of 1 mL of the sample was removed and acidified with 5 μL of FA and directly analyzed without solid phase extraction (SPE) for the parent HBQ and the products using the HPLC-MS/MS (TripleTOF). Triplicate experiments were performed to confirm the identification of the products.

2.5. Analytical Methods. The pH of the water samples was measured with an Accumet model 15 pH meter. The absorbance of each HBQ solution and control sample was measured with a UV/vis spectrometer (Lambda 35, Perkin-Elmer). HBQs were extracted from water using SPE with Waters Oasis HLB cartridges (6 mL, 200 mg per cartridge; Milford, MA). Details of the SPE method are described in the Supporting Information. The parent HBQs were analyzed using the HPLC-MS/MS method as described previously.[22] Briefly, an Agilent 1100 LC (Waldbronn, Germany) with a Luna C18(2) column (100 × 2.0 mm i.d., 3 μm; Phenomenex, Torrance, CA) was used to separate the four HBQs at room temperature. The mobile phase was composed of solvent A (0.25% FA in water) and solvent B (0.25% FA in methanol). The flow rate was 0.17 mL/min, and the sample injection volume was 30 μL. Gradient elution was as follows: linearly increased B from 20% to 90% in 20 min; kept at 90% of B for 5 min; returned to 20% of B for column equilibration at 25.1−40 min. A triple quadrupole tandem mass spectrometer (API 5000, AB Sciex, Concord, ON, Canada) was used for the quantification of the four HBQs. Negative electrospray ionization with MRM mode was used. Optimized MS conditions and MRM ion pairs have been described previously.[22,23] Using this SPE-HPLC-MS/MS method, four HBQs at ng L^{-1} levels can be successfully separated and detected for the current study.

To identify the UV-degradation products, a triple quadrupole TOF mass spectrometer (TripleTOF 5600, AB Sciex, Concord, ON, Canada) coupled with the Agilent 1100 LC was used. The LC program was the same as described above. The conditions of the Triple TOF system were as follows: negative ionization mode, ion source voltage of −4500 V, gas I of 60 arbitrary units, gas II of 60 arbitrary units, curtain gas of 25 arbitrary units, source temperature of 650 °C, declustering potential (DP) of −90 V, collision energy (CE) of −10 V, accumulation time of 0.25 s, and full scan range (m/z) of 100−500 Da.

Analyst (version 1.6, AB Sciex) and PeakView (version 1.2.0.3, AB Sciex) were employed to identify and analyze the peaks. To detect as many peaks as possible in the total ion chromatogram (TIC), the width for specific extracted ion chromatogram (XIC) ranges was set to 5 Da, and the whole search scope was set to range from 100 to 300 Da. We used the triple quadrupole TOF mass spectrometer to obtain the accurate mass, isotope pattern, and MS/MS pattern (product ions) for identification of the products.

2.6. Quality Assurance/Quality Control. All glassware and containers used in this study were rinsed with methanol and baked at 180 °C for 6 h prior to use. The dish for the UV-irradiation experiments was filled with Optima water and stirred for 1 h before each set of experiments; water samples were then collected from the dish and analyzed to ensure there was no contamination (HBQ-free). Method blank samples consisting of Optima water/methanol with 0.25% FA were also analyzed to detect any contamination during LC-MS/MS analysis.

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3. RESULTS AND DISCUSSION

3.1. Absorption Spectra of Four Halobenzoquinones.

The molar absorptivities of DCBQ, DCMBQ, TCBQ, and

Table 1. Estimates of Quantum Yield for Photoproduction of HBQs from OH-HBQs

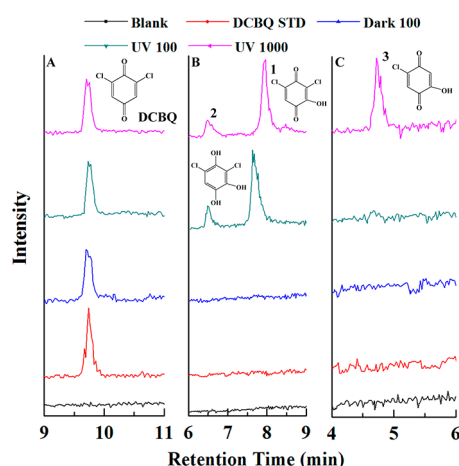| compound	quantum yields (mol Einstein^{-1})	R^2
DCBQ	0.580 ± 0.039	0.925
DCMBQ	0.275 ± 0.028	0.966
TCBQ	0.547 ± 0.035	0.919
DBBQ	0.647 ± 0.026	0.881

Figure 2. XIC results (TOF mass, negative ESI mode) of DCBQ solutions with different treatments. PeakView was employed to identify the peaks at different m/z ranges. A: m/z range from 170 to 180; B: m/z range from 190 to 200; C: m/z range from 150 to 160. The treatments included five conditions. Blank: Optima water solution; DCBQ STD: DCBQ pure solution with concentration of 0.5 μmol L^{-1}; Dark 100: dark reaction during the period equals to the time that UV dose reaches to 100 mJ cm^{-2}; UV 100: UV dose = 100 mJ cm^{-2}; UV 1000: UV dose = 1000 mJ cm^{-2}.

DBBQ in Optima water are shown in Figure S4, Supporting Information. DCMBQ has the strongest absorbance of the four HBQs at 254 nm wavelength, with a molar absorptivity of 6882 M^{-1} cm^{-1}. DBBQ is a relatively weak absorber with a molar absorptivity as low as 2828 M^{-1} cm^{-1}, while DCBQ and TCBQ have moderate absorbing capacity of 4258 and 4449 M^{-1} cm^{-1}, respectively. Optima water has very weak absorbance, which indicates its interference with the UV absorbance of the HBQs is minimal. Thus, it is feasible for these HBQs to experience UV photochemical transformations at the target wavelengths. In addition, these four compounds absorb even more strongly at other wavelengths, especially in the range of 270−280 nm. Therefore, we suggest future studies use other sources of UV radiation than low-pressure Hg lamps to investigate the photodegradation of HBQ compounds.

3.2. Photolysis of Four Halobenzoquinones in Water Irradiated by UV$_{254}$.

Figure 1 shows that all four HBQ compounds were susceptible to UV$_{254}$ degradation in both Optima water and tap water. In Optima water (Figure 1A), over 90% of the four HBQs was degraded after UV$_{254}$ exposure at a dose of 200 mJ cm^{-2}. Among the four HBQs, DCMBQ was the most sensitive to UV$_{254}$ and up to 95% was degraded at a UV$_{254}$ dose less than 100 mJ cm^{-2}. All HBQs tested showed a strong UV dose-dependent relationship; the removal efficiency

Table 2. Transformation Products from Four HBQs by UV$_{254}$ Irradiation

Parent HBQs	Transformation products		
	Hydroxylated HBQs (Peak 1)	Halo-benzenetriols (Peak 2)	Dechlorinated OH-HBQs (Peak 3)

of HBQs increased with the increase of the UV$_{254}$ dose. HBQs were barely detectable after exposure to UV$_{254}$ at 1000 mJ cm^{-2}.

The UV-induced removal rates of the four HBQs in the tap water samples were similar (Figure 1B). Approximately 80% of the four HBQs were removed at a UV$_{254}$ dose of 50 mJ cm^{-2}, while less than 10% of individual HBQs remained in the solutions when the UV dose reached 200 mJ cm^{-2}. Due to the higher absorbance of tap water, the UV-induced removal rates of HBQs are slightly slower in tap water compared to those in Optima water. It should be noted that HBQs were also degraded in the control samples in the dark. The control samples in tap water without UV irradiation degraded approximately 20%, while the control samples in Optima water degraded approximately 10% during the experimental period (2500 s). This is likely due to the effects of reactive components in tap water (Table S2, Supporting Information).

On the basis of the results in Figure 1, the quantum yields at 254 nm (Φ254) of the photodecay of four HBQs were estimated using the nonlinear fitting methods reported previously.[16,24] Table 1 presents the Φ254 values of DCBQ, DCMBQ, TCBQ, and DBBQ. DCMBQ shows the lowest quantum yield among the four compounds, while DCBQ, TCBQ, and DBBQ have similar Φ254 values.

Full scale water treatment plants have applied a range of UV doses (both medium-pressure UV and low-pressure UV) appropriately from 20 to 180 mJ cm^{-2} during the operation.[9] The results in Figure 1 suggest that the four HBQ compounds
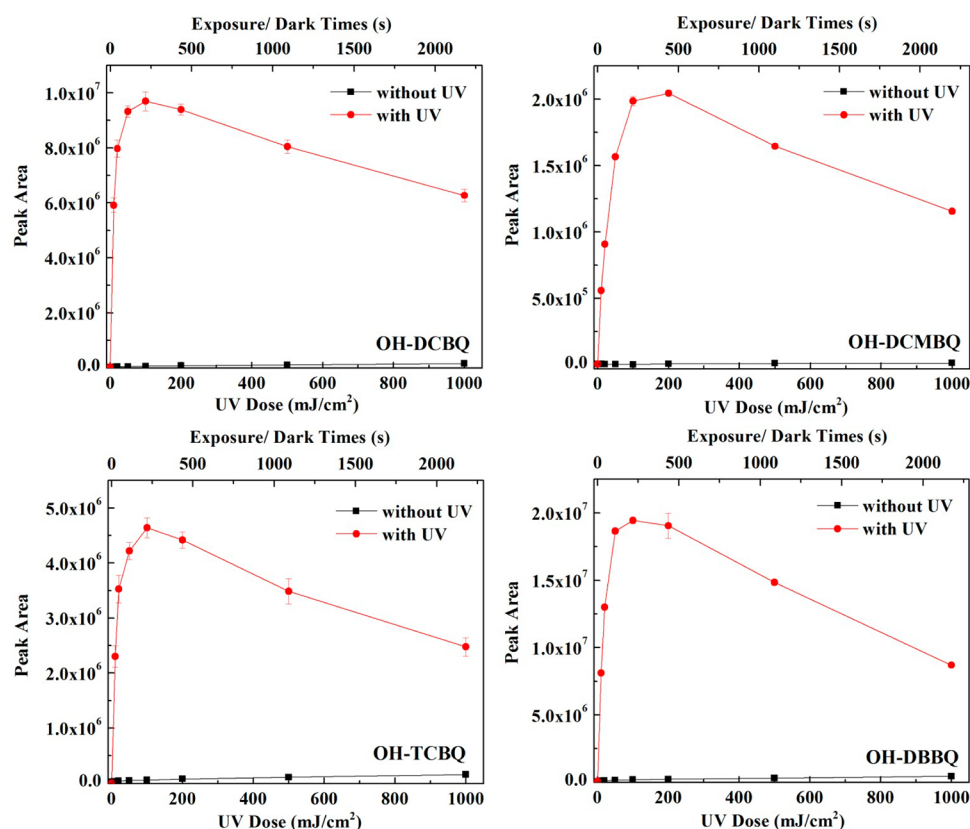
Figure 3. Peak areas of OH-HBQs with and without UV irradiation, showing the formation and degradation of OH-HBQs. Note: Due to lack of standards for OH-HBQs, the amounts of these compounds cannot be quantified.
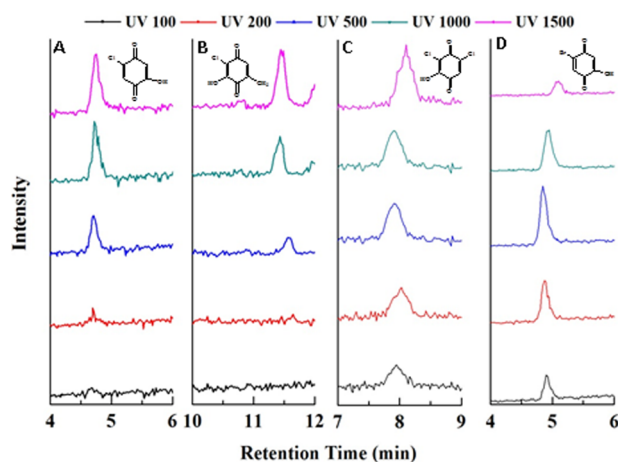

Figure 4. XIC results (TOF mass, negative ESI mode) of dechlorinated/debrominated HBQs under different doses of UV irradiation. A: dechlorinated OH-DCBQ; B: dechlorinated OH-DCMBQ; C: dechlorinated OH-TCBQ; D: debrominated OH-DBBQ.

could be degraded to other products during typical UV treatment. Therefore, the products generated during the UV irradiation process need to be identified.

3.3. Transformation Products of Four Halobenzoqui-nones. We used a high resolution triple quadrupole TOF mass spectrometer to identify the peaks, accurate mass, and MS/MS spectra of the transformation products of HBQs generated from UV irradiation. Here, we use DCBQ as an example to illustrate the identification of its transformation products using

the MS results. Figure 2 shows the XICs of transformation products of DCBQ. Figure 2A shows the parent HBQ, while Figure 2B,C shows XICs of new peaks, which are labeled with a number. Figure 2A shows that DCBQ was detected at the m/z range from 170 to 180, while Figure 2B shows two new peaks (peak 1 and peak 2) detected at the m/z range from 190 to 200 after irradiation with a UV dose of the 100 mJ cm^{-2}. With the increase of UV dose to 1000 mJ cm^{-2}, an additional product (peak 3 in Figure 2C) was detected at a mass range of m/z 150 to 160. Similarly, we obtained the mass spectra of three other HBQs and their transformation products. The results are presented in Figures S5−S7 in the Supporting Information.

Accurate masses and MS/MS spectra were obtained for each of the newly identified peaks (Table S3 and Figure S8, Supporting Information), and structures were proposed for each compound (Table 2). Three main groups of the products were identified: hydroxylated HBQs (OH-HBQs), halo-benzenetriols (HBTs), and dechlorinated/debrominated OH-HBQs produced at higher UV doses. For example, DCBQ was detected to transform to 3-hydroxyl-2,6-dichloro-1,4-benzoqui-none (OH-DCBQ) and 3,5-dichloro-1,2,4-benzenetriol (DCBT) under UV$_{254}$ irradiation for about 4 min (100 mJ cm^{-2}), while dechlorinated DCBQ was detected at higher UV doses (e.g., 1000 mJ cm^{-2}). To further confirm the generation of OH-HBQs and better understand the mechanism of the transformation process, a MRM method was used to determine the peak areas of the four OH-HBQ compounds and to follow their changes in the solutions over the experimental period. Due to lack of the standards of the OH-HBQs and the difference in their ionization efficiency from HBQs, the concentrations of these products cannot be determined.

Scheme 1. Proposed Transformation Pathway of HBQs by UV Irradiation in Water
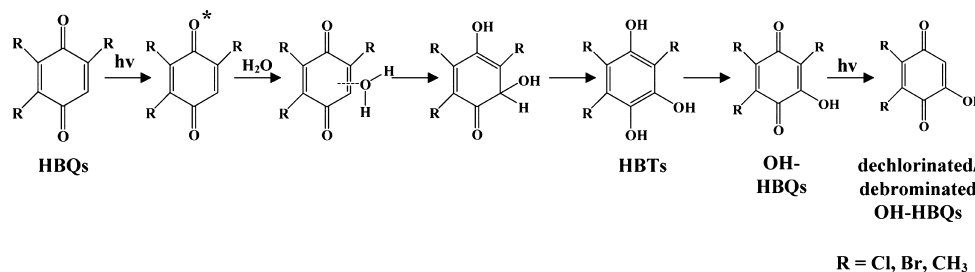
Table 3. Estimates of Quantum Yield for Photodecay of OH-HBQs[a]

compound	quantum yields (mol Einstein^{-1})	R^2
OH-DCBQ	0.0021	0.996
OH-DCMBQ	0.0029	0.999
OH-TCBQ	0.0048	0.969
OH-DBBQ	0.0058	0.997

[a]Calculation is based on the peak areas of OH-HBQs.

Therefore, we use the peak areas to show the change of their concentrations. Table S4, Supporting Information, lists the specific MRM ion transitions and optimized parameters of OH-DCBQ, 5-hydroxyl-2,6-dichloro-3-methyl-1,4-benzoquinone (OH-DCMBQ), 5-hydroxyl-2,3,6-trichloro-1,4-benzoquinone (OH-TCBQ), and 3-hydroxyl-2,6-dibromo-1,4-benzoquinone (OH-DBBQ). Using this method, four OH-HBQs were successfully separated and detected. Also, it should be noted that the detection of OH-HBQs in the treated water samples requires a new SPE method specific for these compounds. Figure 3 shows that the peak areas of all four OH-HBQ compounds varied during UV irradiation. In non-UV irradiated control samples, small peak areas of OH-HBQs were detected and they increased slightly over the experimental period. This indicates that HBQ solutions can have small amounts of OH-HBQs without UV irradiation. Under UV irradiation, the concentrations of OH-HBQs in the treated samples were significantly higher than in the controls without UV irradiation. Figure 3 also shows that the formation rates of the four OH-HBQ compounds are similar under the conditions investigated. The formation (peak area) of OH-HBQs (Figure 3) is correlated with the decrease of the parent compound HBQs (Figure 1) under the UV dose range of 0 to 100 mJ cm^{-2}. Under higher UV doses from 100 to 1000 mJ cm^{-2}, the peak areas of OH-HBQs decreased, suggesting that these products can be further degraded. OH-DCMBQ showed a slight difference from the other three compounds as its maximum amount was detected at UV dose of 200 mJ cm^{-2}.

The phenomenon of a continuing decrease in the peak areas of OH-HBQs suggested that further transformation has occurred with higher UV doses. As shown in Figure 2C and Figures S5C to S7C, Supporting Information, dechlorinated/debrominated OH-HBQs (peak 3) were detected in these solutions under high UV irradiation. Specifically, dechlorinated OH-DCBQ (Figure 2C) and dechlorinated OH-DCMBQ (Figure S5C, Supporting Information) were only found when UV$_{254}$ exposure reached the dose of 1000 mJ cm^{-2}. This observation suggested that the continuous input of energy promoted further transformation of OH-HBQs to dechlorinated/debrominated OH-HBQs. Photodehalogenation of aromatic and heterocyclic compounds has been described in

many publications,[25−27] which supported that chlorine/bromine can be removed from the benzene ring by the input of UV energy in this study. Figure 4 shows the XIC of dechlorinated/debrominated HBQs under different doses of UV irradiation. For DCBQ, DCMBQ, and TCBQ solutions, the peak areas of dechlorinated compounds increased with the enhancement of UV dose. However, the generation of debrominated OH-DBBQ showed a decreasing trend when the UV dose increased from 500 to 1500 mJ cm^{-2}, suggesting further degradation to smaller compounds under high UV doses.

A pathway of HBQ transformation from UV irradiation is proposed in Scheme 1. There is little information in the literature about the photodecay of HBQs, but several studies have investigated the photodecay of different quinones. Lente and Espenson [28] suggested that quinones might have similar photoreaction characteristics due to similar properties of these compounds; thus, it is reasonable to propose that the transformation pathway of the four HBQs in this study may be similar to that of benzoquinones. Benzoquinone (BQ) compounds have been shown to photodecay to 1,2,4-benzenetriol, hydroxylated quinone, and hydroquinone under different experimental conditions.[29−31] According to the spin trapping theory,[32] the excited-state BQ traps hydrogen atoms from water and produces a hydroxyl radical (OH·) in the solution during the irradiation period. OH· can attack BQ itself to produce hydroxylated quinone and hydroquinone. However, Pochon et al.[33] reported that OH· was not produced during photoreaction and an excited state quinone−water intermediate could be generated and then collapsed to 1,2,4-benzenetriol, subsequently transformed to hydroxylated quinone and hydroquinone by an oxidation−reduction reaction with ground-state BQ.[34] Moreover, Gan et al.[35] pointed out that, at high concentrations (larger than 2 mM) of methyl-benzoquinone (MBQ), the excited quinone and ground state quinone could undergo a bimolecular reaction and finally decompose to hydroxylated quinone and hydroquinone, while at low MBQ concentrations, water was the prior reagent to react with excited MBQ to form 3-methyl-1,2,4-benzenetriol, which then transformed to the same products. In this study, the concentrations of four HBQs were as low as 0.5 μmol L^{-1}; thus, the excited HBQs would preferentially react with water to undergo certain reactions to form a HBQ−water exciplex. This HBQ−water complex at excited state was then suggested to collapse to HBTs, which could react further with the ground-state HBQs to form OH-HBQs by an oxidation−reduction reaction. With continuous UV irradiation, these generated OH-HBQs could lose a chlorine or bromine through a substitution reaction and finally form dechlorinated/debrominated OH-HBQs in solution. In addition, the variations of the peak areas (concentrations) of OH-HBQs (Figure 3) revealed that the

initial step in this process (HBQs transform to OH-HBQs) is relatively rapid and the second photochemical step (dehalogenation of OH-HBQs) is relatively slow (Figure 3). The quantum yields and R^2 values for each OH-HBQ were calculated on the basis of the peak areas (Figure 3), and the data is listed in Table 3. It seems that the model fits the data well and the values of $\Phi254$ for all the OH-HBQs are below 1%, which confirms that the dehalogenation step in this process is slow.

In conclusion, HBQs can be transformed by UV_{254} irradiation. Over 80% of initial HBQs were removed by UV_{254} irradiation at typical doses used in water treatment plants. The major transformation products were identified as hydroxylated HBQs (OH-HBQs). However, halo-benzenetriols and monohalogenated benzoquinones were also observed. Further investigation on toxicity studies of OH-HBQs are required to understand the potential risk of these compounds to human health.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figure S1, the setup of the UV device. Table S1, a correction procedure of UV irradiance and relevant data. Table S2, the physical characteristics of tap water and Optima water. Figures S2 and S3, photodecay of four halobenzoquinone at high concentrations (0.5 μmol L^{-1}) in single standard solutions and mixtures after UV_{254} treatments. Figure S4, the molar absorptivity of HBQs in Optima water solution. Figures S5 to S7, the XIC results (TOF mass, negative ESI mode) of DCMBQ, TCBQ, and DBBQ solutions with different treatments. Table S3 and Figure S8, accurate mass and MS/MS patterns of different compounds. Table S4, a MRM method of four OH-HBQs. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*Telephone: (780) 492-5094; fax: (780) 492-7800; e-mail: xingfang.li@ualberta.ca.

Author Contributions
[#]Y.Q. and W.W. contributed equally to this study.

Notes
The authors declare no competing financial interest.

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