Reactivity of BrCl, Br$_2$, BrOCl, Br$_2$O, and HOBr Toward Dimethenamid in Solutions of Bromide + Aqueous Free Chlorine

John D. Sivey,[†,⊥] J. Samuel Arey,[‡,§] Peter R. Tentscher,[‡] and A. Lynn Roberts[†,*]

[†]Department of Geography and Environmental Engineering, Johns Hopkins University, 313 Ames Hall 3400 North Charles Street Baltimore, Maryland 21218, United States

[‡]Environmental Chemistry Modeling Laboratory, Swiss Federal Institute of Technology at Lausanne (EPFL) 1015 Lausanne, Switzerland

[§]Department of Environmental Chemistry, Swiss Federal Institute of Aquatic Science and Technology (Eawag) 8600 Dubendorf, Switzerland

[⊥]Department of Chemistry, Towson University, Smith Hall 543 8000 York Road Towson, Maryland 21252, United States

Ⓢ *Supporting Information*

ABSTRACT: HOBr, formed via oxidation of bromide by free available chlorine (FAC), is frequently assumed to be the sole species responsible for generating brominated disinfection byproducts (DBPs). Our studies reveal that BrCl, Br$_2$, BrOCl, and Br$_2$O can also serve as brominating agents of the herbicide dimethenamid in solutions of bromide to which FAC was added. Conditions affecting bromine speciation (pH, total free bromine concentration ([HOBr]$_T$), [Cl$^-$], and [FAC]$_o$) were systematically varied, and rates of dimethenamid bromination were measured. Reaction orders in [HOBr]$_T$ ranged from 1.09 ($\pm$0.17) to 1.67 ($\pm$0.16), reaching a maximum near the pK_a of HOBr. This complex dependence on [HOBr]$_T$ implicates Br$_2$O as an active brominating agent. That *bromination* rates increased with increasing [Cl$^-$], [FAC]$_o$ (at constant [HOBr]$_T$), and excess bromide (where [Br$^-$]$_o$>[FAC]$_o$) implicate BrCl, BrOCl, and Br$_2$, respectively, as brominating agents. As equilibrium constants for the formation of Br$_2$O and BrOCl (aq) have not been previously reported, we have calculated these values (and their gas-phase analogues) using benchmark-quality quantum chemical methods [CCSD(T) up to CCSDTQ calculations plus solvation effects]. The results allow us to compute bromine speciation and hence second-order rate constants. Intrinsic brominating reactivity increased in the order: HOBr $\ll$ Br$_2$O < BrOCl $\approx$ Br$_2$ < BrCl. Our results indicate that species other than HOBr can influence bromination rates under conditions typical of drinking water and wastewater chlorination.
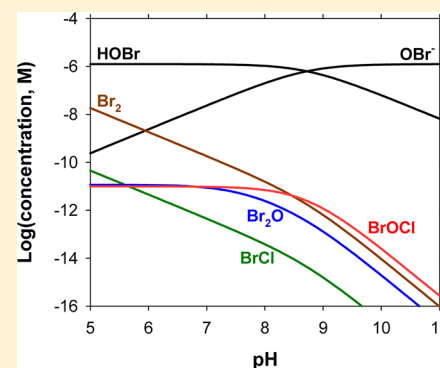
INTRODUCTION

The presence of bromide in waters undergoing chlorine disinfection can result in the formation of brominated disinfection byproducts (DBPs).[1−3] Brominated DBPs are of concern due to their elevated toxicity relative to many of their chlorinated analogues.[4] Understanding the formation pathways of brominated DBPs may help in minimizing their generation; this requires a comprehensive understanding of the chemistry of aqueous brominating agents.

In solutions of free available chlorine (FAC), bromide is rapidly oxidized[5] yielding HOBr and OBr$^-$ as the major products:

$$HOBr \rightleftharpoons OBr^- + H^+$$

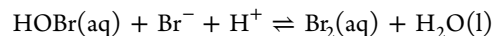$$pK_1 = 8.70(20\ ^\circ C,\ 0\ M\ ionic\ strength,\ ref\ 6) \quad (1)$$
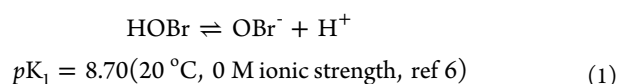
HOBr and OBr$^-$ are not necessarily the only bromine species formed in solutions of bromide and FAC. For example, the near-ubiquitous presence of chloride facilitates formation of bromine chloride (BrCl):

$$HOBr(aq) + Cl^- + H^+ \rightleftharpoons BrCl(aq) + H_2O(l)$$
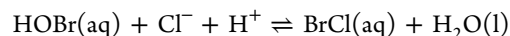
$$\log K_2 = 4.09(20\ ^\circ C,\ 0\ M\ ionic\ strength,\ ref\ 7) \quad (2)$$

Similarly, when [Br$^-$]$_o$ > [FAC]$_o$, bromide can react with HOBr to form molecular bromine (Br$_2$):

$$HOBr(aq) + Br^- + H^+ \rightleftharpoons Br_2(aq) + H_2O(l)$$

$$\log K_3 = 8.40(20\ ^\circ C,\ 0\ M\ ionic\ strength,\ ref\ 8) \quad (3)$$

Br$_2$ and BrCl are frequently overlooked when bromination reactions are discussed in the environmental literature. An important exception is the work of Voudrias and Reinhard,[9,10] who determined Br$_2$ and BrCl to be a factor of 2300 and 4.9 × 10^6, respectively, more reactive than HOBr in brominating *p*-xylene.
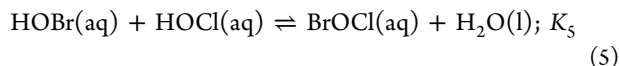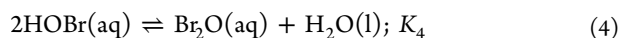
Additional brominating agents[11] (specifically Br_2O and $BrOCl$) can also form when bromide-containing waters are chlorinated:

$$2HOBr(aq) \rightleftharpoons Br_2O(aq) + H_2O(l); \quad K_4 \qquad (4)$$

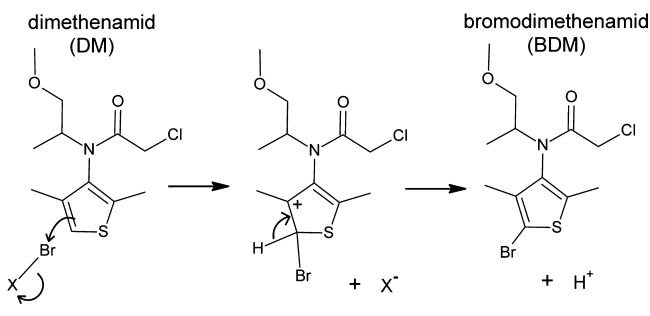$$HOBr(aq) + HOCl(aq) \rightleftharpoons BrOCl(aq) + H_2O(l); \quad K_5 \qquad (5)$$

As OCl^- ($pK_b = 6.42$) is a better leaving group than OBr^- ($pK_b = 5.30$), $BrOCl$ should serve as a brominating agent. In addition to dehydration reactions (eqs 4 and 5), $Br(I)$-transfer from $BrCl$ to OBr^- and to OCl^- may also generate Br_2O and $BrOCl$, respectively.[11]

Br_2O and $BrOCl$ have been characterized in the gas phase via UV−vis absorption spectroscopy.[12−14] Br_2O has also been identified within stratospheric aerosols, including ice[15] and sulfuric acid droplets.[16] To our knowledge, no previous studies have demonstrated the ability of $BrOCl$ or Br_2O to influence rates of DBP precursor bromination. Their omission from prior consideration may reflect the absence of any experimentally or computationally derived stability constants governing their formation in aqueous solution (e.g., K_4 and K_5).

Despite the tendency in the literature to implicate HOBr as the predominant brominating agent of DBP precursors (e.g., refs 2 and 17), HOBr is likely to be inherently less reactive than most of the other bromine species described above. In electrophilic aromatic substitutions involving HOBr, OH^- must be expelled as the leaving group (Scheme 1). OH^- is anticipated to be a poorer

Scheme 1. Postulated Mechanism of Dimethenamid Reaction with Brominating Agents of the Form XBr, Where $X^- = HO^-$, O^{2-}, Cl^-, Br^-, BrO^-, ClO^-

leaving group than Cl^- (from $BrCl$), OCl^- (from $BrOCl$), OBr^- (from Br_2O), and Br^- (from Br_2). As leaving group ability increases, the electrophilicity of the halogenating atom is anticipated to increase, which may also contribute to enhanced rates of bromination. Accordingly, despite the low concentrations anticipated for $BrCl$, $BrOCl$, Br_2O, and Br_2 under drinking water (DW) treatment conditions, we hypothesize that these potentially potent brominating agents can influence rates of DBP precursor bromination in much the same way that Cl_2O and Cl_2 have been shown to represent more reactive chlorinating agents of organic compounds than is HOCl.[9,18,19]

The goal of the current work is to delineate the contributions of individual bromine species (HOBr, $BrCl$, $BrOCl$, Br_2O, and Br_2) during bromination of the widely used[20] herbicide dimethenamid (DM). DM was selected for study because this molecule: (1) has been identified in surface waters,[21] as well as in finished DW;[22] (2) was previously demonstrated to react with FAC and free bromine to yield electrophilic aromatic substitution products in high yield;[18,23] and (3) lacks ionizable groups (as does its halogenation products), thereby simplifying

speciation assignments. The effects of several independent variables on rates of DM bromination are examined, including pH, [FAC], $[Cl^-]$, total free bromine concentration ($[HOBr]_T$), [buffer], and ionic strength. To enable quantitative comparisons of the reactivity of different brominating agents, equilibrium constants for the formation of Br_2O and $BrOCl$ were computed using quantum chemistry. By quantifying the reactivities of several bromine species (as opposed to only HOBr), the current work provides a more comprehensive framework with which to assess bromination rates of DBP precursors.

EXPERIMENTAL SECTION

A description of reagents, including standardization of and measurements of chloride in FAC solutions is provided in Supporting Information (Table S1).

Kinetic Experiments. Reactors consisted of 40 mL amber glass vials with Teflon-lined caps; vials were rinsed with FAC solution (0.43 mM) and distilled/deionized water before use. Reactors were prepared by combining borate or phosphate buffer (10 mM), supporting electrolyte ($NaNO_3$), and NaBr (100 − 400 μM) to give a total solution volume of 25 mL. FAC working solution was added to each reactor to give total initial FAC concentrations ($[FAC]_o$) of 100−430 μM. Vials were capped, shaken, and placed in a water bath (20.0 ± 0.1 °C) for ~4 min to permit oxidation of bromide. In the absence of excess bromide (where $[Br^-]_{xs} = [Br^-]_o − [FAC]_o$), >99% of added Br^- is calculated to be oxidized within 4 min at the pH values (7.3−10.2) examined herein.[5] Excepting reactions in solutions dosed with excess bromide, total bromine concentration ($[HOBr]_T = [HOBr] + [OBr^-] + [BrCl] + [Br_2] + [BrOCl] + [Br_2O]$) was assumed equal to $[Br^-]_o$. For reactions in solutions dosed with excess bromide, $[HOBr]_T$ was assumed equal to $[FAC]_o$. DM was added at $t = 0$ as an aqueous spike to give $[DM]_o = 8$ μM. Vials were immediately capped, shaken vigorously, and returned to the water bath. Reactors were periodically sampled by placing 0.80 mL of reaction solution into 4 mL glass vials prespiked with sodium thiosulfate ([thiosulfate]/$[FAC]_o$ ~1.6) to quench bromine and chlorine; toluene (0.40 mL), containing propachlor (14 μM) as an internal standard, was added as an extraction solvent. After the final sample was obtained, solution pH was measured (Accumet AR 15, Fisher Scientific, calibrated daily using standards at pH 4.00, 7.00, and 10.00). Measurements of pH in selected samples prior to addition of DM indicated that solution pH varied by ≤0.02 units over the course of reactions.

Variable Solution Condition Experiments. Variables that affect bromine speciation include pH, $[HOBr]_T$, $[FAC]_o$, $[Cl^-]$, $[Br^-]_{xs}$, and ionic strength. Experiments evaluating these solution conditions are described in section 3 and Figure S1 of the Supporting Information. Experiments were also performed in which buffer concentrations were varied from 6 to 60 mM. The concentration of borate buffer had no discernible influence on rates of DM bromination (Figure S2 of the Supporting Information). Bromination rates did, however, increase with increasing phosphate concentration (Figure S2), as discussed further in the Supporting Information. To avoid this complication, all experiments discussed hereafter were performed in borate buffer.

Analysis of DM and Transformation Products. Qualitative analysis of toluene extracts was performed on a gas chromatograph (GC) interfaced with a mass spectrometer (MS). A single product (BDM, Scheme 1) was observed in all extracts. The analogous chlorinated product of DM was not observed, which is consistent with the generally lower halogenation

reactivity of chlorine versus bromine.[24] Quantitative analysis of DM and BDM was performed by analyzing toluene extracts on a GC with a microelectron capture detector. Additional details of the GC methods are provided in Table S2 of the Supporting Information.

Modeling of Kinetic Data. All experiments were performed under pseudo-first-order conditions in which $[HOBr]_T/[DM]_o \geq 12$. Complete carbon mass balances ($[DM] + [BDM]$) were observed (example time courses, Figure S3 of the Supporting Information). Reactions could be monitored to completion, and reaction rates could be described by:

$$\text{rate} = -\frac{d[DM]}{dt} = \frac{d[BDM]}{dt} = k_{obs}[DM] \qquad (6)$$

Reaction rate constants (k_{obs}) were calculated from the slopes of $\ln[DM]$ versus time plots; these plots were consistently linear through at least three half-lives (data not shown), indicating that reactions were first-order in $[DM]$.

Equilibrium Constants for Br$_2$O, BrOCl, and Cl$_2$O. Equilibrium constants (K_{eq}) have been reported previously[25] for the aqueous-phase formation of Cl$_2$O (eq 7) but not for Br$_2$O (eq 4) or BrOCl (eq 5).

$$2HOCl(aq) \rightleftharpoons Cl_2O(aq) + H_2O(l); \log K_7 = -2.06 \qquad (7)$$
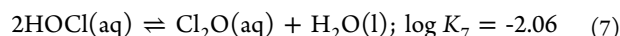
Equilibrium constants for eqs 4, 5, and 7 were determined using benchmark-quality quantum chemistry methods, described below. Calculations for Cl$_2$O were included to permit method validation. Although kinetic experiments were performed at 20 °C (to permit comparisons with previous work[9,10]), quantum computations of equilibrium constants assume 25 °C, because the solvation-modeling protocol only treats solutes at 25 °C. This temperature discrepancy is estimated to contribute ≤10% uncertainty for K_4 and K_5 (Supporting Information).

Previous theoretical work[26−28] indicates that core−valence electron correlation effects and electronic relativistic effects contribute significantly to the enthalpy of formation for oxides of chlorine and bromine. Additionally, post-CCSD(T) excitations contribute to total atomization energies of some chlorine oxides[27] and therefore post-CCSD(T) contributions may also be expected for bromine analogues. Second-order molecular spin−orbit contributions to the atomization energies have been shown to vary by <1 kJ/mol among the diatomic series HBr, FBr, and ClBr;[29] therefore this effect was estimated to contribute <1 kJ/mol to the enthalpies of homodesmic reactions 4, 5, and 7.

On the basis of these considerations, we computed gas-phase thermochemistry using high-quality theoretical calculations expected to have kJ/mol-level prediction skill[27,29−31] for $\Delta H_{rxn,298}$, with the *Gaussian09*[32] and *CFOUR*[33]/*MRCC*[34] softwares, as follows. Geometries were optimized using all-electron CCSD(T)[35] with the aug-cc-pVTZ basis set[36−38] or were taken from theoretical benchmarks.[27,39] On these geometries, electronic energies were computed using CCSD(T) extrapolated to infinite basis set[40] with aug-cc-pVQZ and aug-cc-pV5Z[36−38] and were corrected for higher order CCSDT,[41,42] CCSDT(Q),[43] and CCSDTQ[44] excitations using cc-pVQZ, cc-pVQZ, and cc-pVDZ, respectively.[30,40,45] Core/valence correlation effects were computed using CCSD(T)/aug-cc-pwCVQZ.[46,47] Scalar relativistic effects were evaluated[48,49] using CCSD(T)/aug-cc-pV5Z-DK.[50] Rotational constants were calculated from all-electron CCSD(T)/aug-cc-pCVTZ geometries. Frequencies were obtained via an additivity approximation[31] to the anharmonic, core-correlated CCSD(T)/aug-cc-pCVQZ result. Gas-phase results were then adjusted for aqueous solvation effects using a variant of the cluster-continuum approach.[51] The resulting computed aqueous equilibrium constants for eqs 4, 5, and 7 were expected to have factor-of-two uncertainty (all uncertainty estimates herein denote 95% confidence intervals). These methods are explained further in section 7 and Table S3 of the Supporting Information.

■ RESULTS AND DISCUSSION

Quantum-Computed Equilibrium Constants. Computed thermochemical parameters for the gas-phase and aqueous-phase hydration of Br$_2$O, BrOCl, and Cl$_2$O (eqs 4, 5, and 7, respectively) are provided in Table 1 along with previously reported values. For the gas-phase hydration of Cl$_2$O, quantum-chemical calculations agree well with previous theoretical and experimental estimates of $\Delta H_{rxn,298}$ and $\Delta G_{rxn,298}$. Our calculations also agree with previous experimental data for the aqueous-phase hydration of Cl$_2$O[25] indicating that the quantum-chemical model also correctly treated aqueous solvation effects.

For the gas-phase hydration of BrOCl, our computed $\Delta H_{rxn,298}$ (−10.2 kJ/mol) corroborates an independent estimate obtained using high-quality $\Delta H_{f,298}$ data (−10.1 kJ/mol).[26,28,52] For the gas-phase hydration of Br$_2$O, discrepancies exist among $\Delta H_{rxn,298}$ estimates. Aguzzi and Rossi[15] proposed a value of −15 kJ/mol based on estimated $\Delta H_{f,298}$ values for Br$_2$O, HOBr, and H$_2$O. Using improved $\Delta H_{f,298}$ estimates from more recent literature,[26,28,52] we derived an updated $\Delta H_{rxn,298}$ of −9.7 kJ/mol, in close agreement with our computed value of −10.4 kJ/mol.

Table 1. Thermodynamic Properties of Cl$_2$O, Br$_2$O, and BrOCl Formation from HOCl and HOBr in Both Gas and Aqueous Phase

Reaction	Thermochemistry Values Based on Previously Reported Data			Thermochemistry Values of the Present Work		
	$\Delta H_{rxn,298}$ (kJ mol^{-1})	$\Delta G_{rxn,298}$ (kJ mol^{-1})	log K_{eq}	$\Delta H_{rxn,298}$ (kJ mol^{-1})	$\Delta G_{rxn,298}$ (kJ mol^{-1})	log K_{eq}
2HOCl (g) ⇌ Cl$_2$O (g) + H$_2$O (g)	−10.8 ± 0.7[a], −11[b]	−5.9 ± 0.3[c]	1.04 ± 0.05[c]	−10.5	−5.6	0.98
2HOBr (g) ⇌ Br$_2$O (g) + H$_2$O (g)	−15[b], −9.7[d]	−9.7[e]	1.70[e]	−10.4	−5.6	0.97
HOCl (g) + HOBr (g) ⇌ BrOCl (g) + H$_2$O (g)	−10.1[d]	not reported	not reported	−10.2	−7.1	1.25
2HOCl (aq) ⇌ Cl$_2$O (aq) + H$_2$O (l)	0.6[f]	11.7[g]	−2.06[g]	not determined	10.4	−1.82
2HOBr (aq) ⇌ Br$_2$O (aq) + H$_2$O (l)	not reported	not reported	not reported	not determined	−4.6	0.80
HOCl (aq) + HOBr (aq) ⇌ BrOCl (aq) + H$_2$O (l)	not reported	not reported	not reported	not determined	2.6	−0.46

[a]Determined using the computed $\Delta H^0_{f,298}$ values of HOCl and Cl$_2$O reported by ref 27 and the experimental $\Delta H^0_{f,298}$ value of H$_2$O reported in ref 52. [b]Estimates by ref 15. [c]Experimental value from ref 53. [d]Determined using the computed $\Delta H^0_{f,298}$ values of HOCl and HOBr reported in ref 26, the computed $\Delta H^0_{f,298}$ values of Br$_2$O and BrOCl reported by ref 28, and the experimental $\Delta H^0_{f,298}$ value of H$_2$O reported ref 52. [e]Experimental value from ref 12. [f]Experimental value from ref 54. [g]Experimental value from ref 25, corrected to 25 °C from ref 54.

For $\Delta G_{rxn,298}$ of Br_2O hydration, Orlando and Burkholder[12] report a value of −9.7 kJ/mol, in disagreement with our quantum-chemical value of −5.6 kJ/mol. Orlando and Burkholder[12] estimated an equilibrium constant based on measured concentrations of Br_2O, HOBr, and H_2O using a steady-state reactor, which may or may not have guaranteed equilibrium conditions. On the basis of the previous accuracy of coupled cluster calculations for gas-phase thermochemistry,[27,29] our successful corroboration of the best independent estimate of $\Delta H_{rxn,298}$ for Br_2O, and our successful prediction of gas-phase vibrational frequencies (over all species, average deviation was 5 cm^{-1} and maximum deviation was 20 cm^{-1}, compared to experiment), we conclude that our computed gas-phase $\Delta G_{rxn,298}$ value for Br_2O represents an improved estimate over that reported by Orlando and Burkholder.[12]

Overall, the employed quantum-chemical methods produce good agreement with several previous experimental and theoretical results. To our knowledge, this is the first report of aqueous-phase equilibrium constants for hydration of Br_2O (K_4) and BrOCl (K_5) and the first report of gas-phase thermochemistry for hydration of BrOCl. Computed values of K_4 and K_5 were used to construct the aqueous-phase bromine speciation diagram shown in Figure 1.
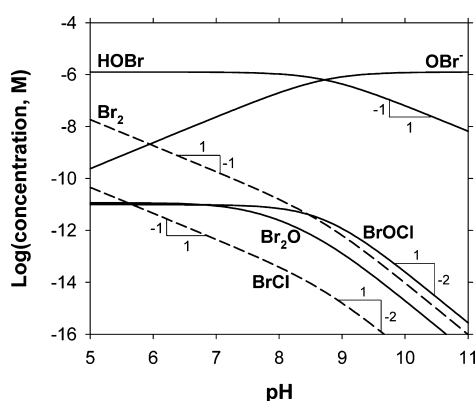

Figure 1. Aqueous bromine equilibrium speciation at 20 °C under typical drinking water chlorination conditions (solid lines): $[Br^-]_o = 1.25 \times 10^{-6}$ M = 100 μg/L (median $[Br^-]$ in DW sources[55]) and $[FAC]_o = 2.8 \times 10^{-5}$ M = 2.0 mg/L as Cl_2). Inclusion of chloride (3.0 × 10^{-4} M = 11 mg/L; median $[Cl^-]$ in DW sources[56]) and excess bromide ($[Br^-]_{xs} = [Br^-]_o - [FAC]_o = 1.0 \times 10^{-6}$ M = 80 μg/L) generates BrCl and Br_2, respectively (broken lines), with no appreciable change to the other species. Concentrations were calculated using eqs 1−5 including values of K_4 and K_5 determined herein (Table 1) via quantum-chemical computations.

Reaction Order in [HOBr]$_T$. The reaction order (n) in $[HOBr]_T$ for DM bromination was determined while maintaining pseudo-first-order conditions ($[HOBr]_T/[DM]_o \geq 12$):

$$k_{obs} = k_{app}([HOBr]_T)^n \tag{8}$$

where k_{app} is a pH-dependent apparent rate coefficient. Values for n were determined via linear regressions of log(k_{obs}) versus log($[HOBr]_T$) under several solution conditions; results are summarized in Figure S4 of the Supporting Information. Values of n increase with increasing pH from 1.22 (±0.16) at pH 8.0 to 1.67 (±0.16) at pH 8.6. Above pH 8.6, n values decrease to 1.09 (±0.17) at pH 9.7. These results suggest concurrent reactions that are first-order and second-order in $[HOBr]_T$ influence rates of DM bromination. Plausible brominating agents

that are first-order in $[HOBr]_T$ include HOBr, OBr^-, BrOCl, and BrCl. Br_2 would also give rise to reactions that are first-order in $[HOBr]_T$ (assuming an electrophilic aromatic substitution mechanism). The lack of excess bromide, however, precludes Br_2 as a significant reactive species in this set of experiments.

Formation of Br_2O as an active brominating agent can account for the near second-order dependence of DM bromination rates on $[HOBr]_T$ observed at pH ~8.6. Analogous reports in the chlorination literature[9,18,19,57,58] have attributed a second-order dependence of chlorination rates on $[FAC]_o$ to reactions with Cl_2O. Indeed, Cl_2O was found to be nearly 8 million times more inherently reactive than HOCl in reactions with DM.[18] As with its chlorine analogue, we postulate that Br_2O is more inherently reactive than HOBr, as discussed below.

Influence of [FAC]$_o$. The effect of varying $[FAC]_o$ (at constant $[HOBr]_T$) on k_{obs} for DM bromination is shown in Figure 2. Note that $[FAC]_o > [HOBr]_T$ for each of these
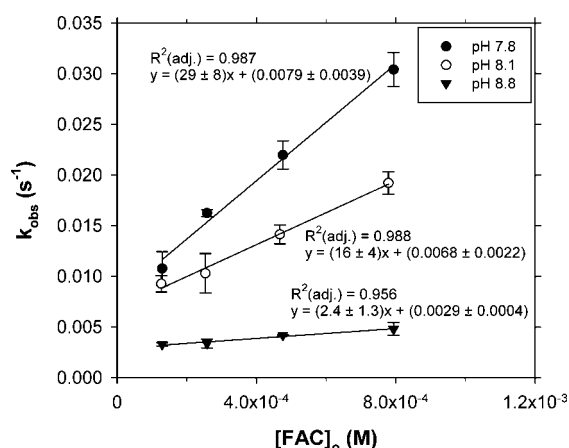

Figure 2. Rate constants for DM bromination as a function of initial free available chlorine concentration ($[FAC]_o$) at pH 7.8, 8.1, and 8.8. Uniform conditions: $[Br^-]_o = 6.1 \times 10^{-5}$ M, $[DM]_o = 4.0 \times 10^{-6}$ M, [borate buffer] = 10 mM, $[NaNO_3]$ = 0.10 M, T = 20.0 ± 0.1 °C. Error estimates denote 95% confidence intervals.

experiments. Nevertheless, the chlorinated product was not detected, and rates of DM loss were equal to rates of BDM formation. At all examined pH values (7.7, 8.1, and 8.8), k_{obs} increases linearly with increasing $[FAC]_o$. The slope of the linear regressions decreases with increasing pH, suggesting the rate enhancement is proportional to [HOCl] rather than [OCl$^-$]. That rates of bromination correlate with *chlorine* dose may seem, at first, counterintuitive. As [BrOCl] is proportional to [HOCl] (eq 5), we posit that formation of BrOCl as an active brominating agent accounts for increases in k_{obs} with increasing $[FAC]_o$. This may explain the findings of Ichihashi et al.[59] who reported increased yields of brominated trihalomethanes from phenolic compounds with increasing $[FAC]_o$ (at fixed $[HOBr]_T$ and pH 8). It is unclear, however, whether BrOCl is responsible for their trend.[59] For example, in natural waters, it is conceivable that higher doses of FAC may result in an increased extent of (re)oxidation of bromide (which could be generated were HOBr to react with certain reductants).

Another potential explanation for observed rate enhancements with increasing $[FAC]_o$ is general-acid catalysis by HOCl. Phosphate buffer was shown to catalyze DM bromination (Figure S2 of the Supporting Information). The slope of the k_{obs} versus [phosphate]$_T$ plot is ~0.5 M^{-1} s^{-1} at pH 7.7 (Figure S2 of

the Supporting Information) and ~30 M^{-1} s^{-1} for k_{obs} versus [FAC]$_o$ at pH 7.8 (Figure 2). If HOCl were serving as a general-acid catalyst, these data imply that HOCl is a more effective catalyst than H$_2$PO$_4^-$. General-acid catalysis, however, typically scales with acid strength.[60] The weaker acidity of HOCl (pK_a = 7.5) and the much lower concentration of HOCl ([FAC]$_o$ = 0.2 − 0.8 mM) relative to H$_2$PO$_4^-$ (pK_a = 7.2, [phosphate]$_T$ = 10 − 40 mM) suggests that HOCl is not acting as a general-acid catalyst. HOBr, with a pK_a of 8.7 and a lower concentration than HOCl, is even less likely to serve as a general-acid catalyst in our experiments.

Effects of pH, Chloride and Excess Bromide. Results of experiments performed at pH values ranging from 7.3 to 10.2 are shown in Figure 3. Under all conditions, k_{obs} values increase with
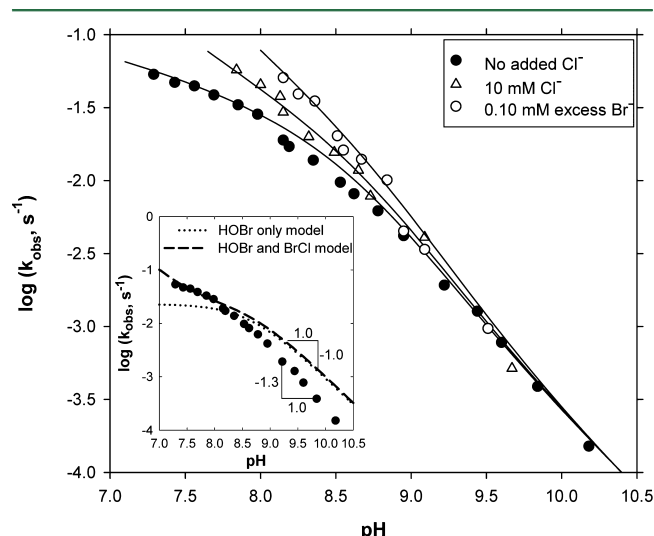

Figure 3. Rate constants for DM bromination as a function of pH. Solid lines denote model fits assuming $k_{obs} = k_{BrCl}[BrCl] + k_{Br_2}[Br_2] + k_{BrOCl}[BrOCl] + k_{Br_2O}[Br_2O] + k_{HOBr}[HOBr]$. Reaction conditions: [DM]$_o$ = 9 μM, [borate buffer] = 10 mM, T = 20.0 ± 0.1 °C. Additional conditions for no added Cl$^-$ and 10 mM (0.35 g/L) Cl$^-$: [FAC]$_o$ = 0.43 mM = 30 mg/L as Cl$_2$, [Br$^-$]$_o$ = 0.10 mM = 8.0 mg/L, [NaNO$_3$] + [NaCl] = 0.1 M. Additional conditions for 0.10 mM excess Br$^-$: [FAC]$_o$ = 93 μM = 6.6 mg/L as Cl$_2$, [Br$^-$]$_o$ = 0.20 mM = 16 mg/L, [NaNO$_3$] = 0.1 M. Model fits shown for no added chloride and 0.10 mM excess Br$^-$ data assume [Cl$^-$] = 0.4 mM = 14 mg/L (Supporting Information for rationale). Insert: Model fits to the "no added Cl$^-$" data assuming only HOBr or both HOBr and BrCl as reactive brominating agents.

decreasing pH. In the absence of added Cl$^-$, k_{obs} values continue to increase even at pH values well below 8.7 (the pK_a of HOBr). This may result from specific-acid catalysis or from reactions with BrCl (generated from low levels of Cl$^-$ present in reaction solutions). We present evidence in Figures S5 and S6 of the Supporting Information indicating specific-acid catalysis does not appreciably influence bromination rates in our systems.

To explore the potential influence of BrCl in this pH range, measurements of k_{obs} were made as a function of pH in reactors amended with Cl$^-$ (10 mM). In these systems, a rate enhancement is observed at pH ≤ 8.5 (Figure 3). BrCl can account for rate enhancements observed with decreasing pH and with increasing [Cl$^-$] (eq 2). Additional experiments were performed at four pH values (8.1, 8.3, 8.5 and 8.7) in which the [Cl$^-$] was varied from 3 to 29 mM (Figure S5 of the Supporting Information). The resulting plots of k_{obs} versus [Cl$^-$] are linear, and the degree of chloride catalysis, indicated by the slope of k_{obs}

versus [Cl$^-$] plots, increases with decreasing pH. Both observations are consistent with BrCl functioning as an active brominating agent.

In reactors amended with 0.10 mM of excess Br$^-$, a rate enhancement is also observed at pH ≤ 8.5 (Figure 3). To further elucidate the effects of excess Br$^-$ on bromination rates, additional experiments were performed at pH 8.5 in which [Br$^-$]$_{xs}$ was varied from 0.10 to 0.26 mM at uniform [FAC]$_o$. An approximately linear increase in k_{obs} was observed with increasing [Br$^-$]$_{xs}$ (data not shown). Catalysis of DM bromination by excess Br$^-$ can be explained by formation of Br$_2$, noting that [Br$_2$] is proportional to [Br$^-$]$_{xs}$ (eq 3). The linear relationship between k_{obs} and [Br$^-$]$_{xs}$ serves as indirect evidence that DM bromination by Br$_2$ does not follow a radical pathway. If bromine radicals were reactive species, a half-order dependence of k_{obs} on [Br$^-$]$_{xs}$ might be expected (as homolysis of Br$_2$ would generate two bromine radicals per mole of Br$_2$).

Modeling of Kinetic Data. An attempt to model the "no added Cl$^-$" data assuming HOBr as the sole reactive species (i.e., $k_{obs} = k_{HOBr}[HOBr]$) is shown in Figure 3 (insert). The HOBr-only model underpredicts k_{obs} at pH < 8.5 and overpredicts k_{obs} at pH > 8.5. Inclusion of BrCl (HOBr + BrCl model in Figure 3) provides improved fits to the data at pH < 8.5, consistent with BrCl serving as an active brominating agent. Inclusion of BrCl does not, however, improve model fits at pH > 8.5. A steeper slope (−1.3) is observed from pH 9.0 to 10.0 than is predicted by the HOBr model (−1). If BrCl, BrOCl, or Br$_2$O were the predominant brominating agent in the pH 9−10 range, a slope approaching −2 is anticipated (Figure 1). That the slope does not appreciably change in the pH 9−10 range upon addition of 10 mM Cl$^-$ (Figure 3) suggests that BrCl is unimportant under these conditions. Br$_2$O and/or BrOCl may, however, be influencing k_{obs} in this pH range.

Attempts were made to model our data (including no added Cl$^-$, 10 mM Cl$^-$ and 0.10 mM excess Br$^-$) assuming the following reactivity model:

$$k_{obs} = k_{BrCl}[BrCl] + k_{Br_2}[Br_2] + k_{BrOCl}[BrOCl] + k_{Br_2O}[Br_2O] + k_{HOBr}[HOBr] \qquad (9)$$

It is useful to rewrite eq 9 noting that [BrCl] = K_2[HOBr][H$^+$][Cl$^-$] (eq 2), [Br$_2$] = K_3[HOBr][H$^+$][Br$^-$] (eq 3), [BrOCl] = K_5[HOBr][HOCl] (eq 5), and [Br$_2$O] = K_4[HOBr]^2 (eq 4):

$$\begin{aligned} k_{obs} = &\; k_{BrCl}K_2[HOBr][H^+][Cl^-] + \\ &\; k_{Br_2}K_3[HOBr][H^+][Br^-]_{xs} + \\ &\; k_{BrOCl}K_5[HOBr][HOCl] + k_{Br_2O}K_4[HOBr]^2 + \\ &\; k_{HOBr}[HOBr] \end{aligned}$$

$$(10)$$

Best estimates for rate constants (k_{BrCl}, k_{Br_2}, k_{BrOCl}, k_{Br_2O} and k_{HOBr}) were obtained via nonlinear least-squares fitting of eq 10 using k_{obs}, [HOBr], [H$^+$], [Cl$^-$], [Br$^-$]$_{xs}$, and [HOCl] computed for each experiment as model input (section 10 of the Supporting Information). The following second-order rate constants (units: M^{-1} s^{-1}) were obtained: k_{BrCl} = (2.1 ± 0.3) × 10^8, k_{Br_2} = (3.8 ± 0.4) × 10^6, k_{BrOCl} = (3.7 ± 1.9) × 10^6, k_{Br_2O} = (4.1 ± 2.2) × 10^5, and k_{HOBr} = (58 ± 15). Inclusion of a specific acid-catalysis term (e.g., $k_{H_2OBr^+}$[H$^+$][HOBr] or $k_{HBr_2O^+}$[H$^+$][HOBr]^2) or a term for hypobromite (k_{OBr^-}[OBr$^-$]) did not improve model fits. As O^{2-} is anticipated to be a less labile leaving group relative to OH$^-$,

Table 2. Rate Constants for Reactions of Brominating and Chlorinating Agents with Dimethenamid (DM) and p-Xylene[a]

species	$k(DM)/M^{-1} s^{-1}$	k/k_{HOBr}	$k(p\text{-xylene})/M^{-1} s^{-1b}$	k/k_{HOBr}	$k(DM)/k(p\text{-xylene})$
BrCl	$(2.1 \pm 0.3) \times 10^{8c}$	3.6×10^6	540 ± 9	4.9×10^6	3.8×10^5
Br$_2$	$(3.8 \pm 0.4) \times 10^{6c}$	6.5×10^4	0.251 ± 0.004	2.3×10^3	1.5×10^7
BrOCl	$(3.7 \pm 1.9) \times 10^{6c}$	1.7×10^4	Not reported	Not reported	
Cl$_2$O	$(1.37 \pm 0.17) \times 10^{6d}$	2.4×10^4	54 ± 4	4.9×10^5	2.5×10^4
Cl$_2$	$(1.16 \pm 0.05) \times 10^{6d}$	2.0×10^4	58 ± 9	5.3×10^5	2.0×10^4
Br$_2$O	$(4.1 \pm 2.2) \times 10^{5c}$	1.1×10^3	Not reported	Not reported	
HOBr	58 ± 15^c	1.0	$(1.1 \pm 0.7) \times 10^{-4}$	1.0	5.3×10^5
HOCl	0.18 ± 0.10^d	3.1×10^{-3}	Not reported	Not reported	

[a]Conditions: 20 °C and 0.1 M ionic strength; error estimates denote 95% confidence intervals. Reported second-order rate constants are only as robust as the corresponding equilibrium constants employed to calculate concentrations of each active brominating and chlorinating agent. [b]Ref 9. [c]Current work. [d]Ref 18.

we anticipate OBr⁻ to be a weaker brominating agent than HOBr. Model predictions from eq 10 provide good fits to all three data sets in Figure 3 (solid lines).

Rate constants for reaction of DM with brominating (current work) and chlorinating[18] agents are summarized in Table 2. The reactivity trend among halogenating agents for which second-order rate constants can be calculated is: HOCl < HOBr < Br$_2$O < Cl$_2$ ≈ Cl$_2$O < BrOCl ≈ Br$_2$ < BrCl. Voudrias and Reinhard[9] observed a similar trend for halogenation of p-xylene: HOCl ≪ HOBr < Br$_2$ < Cl$_2$ ≈ Cl$_2$O < BrCl, differing mainly in the relative importance of Br$_2$. Br$_2$O and BrOCl were reportedly unimportant under the conditions (pH 2.5−7.5) examined by Voudrias and Reinhard.[9]

The reactivity trend among brominating and chlorinating agents suggests that both nucleofugality (leaving group ability) and polarizability can influence reaction rates. For example, even though O−Br bond breaking is involved when HOBr, BrOCl, and Br$_2$O serve as brominating agents, the reactivity trend HOBr < Br$_2$O < BrOCl is consistent with the anticipated trend in leaving group abilities: OH⁻ < OBr⁻ < OCl⁻. The increased reactivity of HOBr relative to HOCl is likely due to the lesser bond dissociation energy (BDE) at 25 °C of O−Br (homolytic BDE = 235 kJ/mol, ref 61) relative to O−Cl (269 kJ/mol, ref 61), assuming trends in heterolytic BDEs parallel those in homolytic BDEs. The greater polarizability and greater partial positive halogen charge of HOBr may also elevate halogenation rates compared to HOCl. Increases in polarizability among electrophiles can facilitate formation of precursor complexes with electron-rich moieties and subsequently increase halogenation rates.[60] Polarizability and bond energy arguments can also explain the increased reactivity of BrCl (BDE = 219 kJ/mol, ref 61) relative to Cl$_2$ (BDE = 242 kJ/mol, ref 61). The greater polarizability of Br$_2$ likely contributes to its greater reactivity relative to Cl$_2$. Voudrias and Reinhard,[9] however, found Br$_2$ to be ~200 times less intrinsically reactive than Cl$_2$ in reactions with p-xylene, which conflicts with the general finding of brominating agents being more intrinsically reactive than chlorinating agents. As bromine atoms are larger than chlorine atoms, steric effects may also influence the relative rates of bromination versus chlorination.

Brominating agents react much more rapidly with DM than with p-xylene. Bromination rate constants with DM are at least a factor of 1.5×10^5 greater than with p-xylene (Table 2) suggesting that the substituted thiophene group of DM is more nucleophilic than p-xylene.

Environmental Significance. The relative contributions of individual brominating agents to the overall transformation of DM under typical drinking water (DW) or wastewater (WW) chlorination conditions are shown in Figure 4. The effects of pH
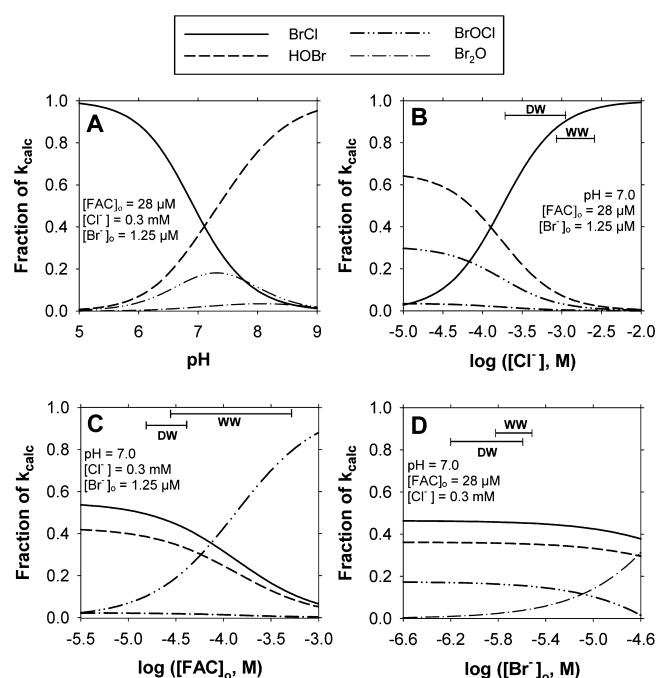

Figure 4. Contributions of brominating agents to DM reactivity (as fraction of k_{calc} at 20 °C, where $k_{calc} = k_{BrCl}[BrCl] + k_{Br_2}[Br_2] + k_{BrOCl}[BrOCl] + k_{Br_2O}[Br_2O] + k_{HOBr}[HOBr]$): (A) as a function of pH under typical DW chlorination conditions {[FAC] = 28 μM = 2 mg/L as Cl$_2$, [Cl⁻] = 0.3 mM = 11 mg/L, and [Br⁻]$_o$ = 1.25 μM = 100 μg/L, the median Cl⁻ (ref 56) and Br⁻ (ref 55) levels respectively in DW sources}; (B) as a function of [Cl⁻] at pH 7.0 and [Br⁻]$_o$ = 1.25 μM. Typical [Cl⁻] in DW (ref 56) and WW (ref 62) are shown. In (C), the effects on k_{calc} of varying [FAC]$_o$ (assuming pH 7.0, [Cl⁻] = 0.3 mM and [Br⁻]$_o$ = 1.25 μM) are depicted. Typical [FAC]$_o$ ranges employed during DW (ref 63) and WW (ref 62) are shown. In (D), the effects on k_{calc} of varying [Br⁻]$_o$ are shown (assuming pH 7.0, [FAC]$_o$ = 28 μM and [Cl⁻] = 0.3 mM). Typical [Br⁻]$_o$ in DW (ref 55) and WW (ref 62) are shown. All k_{calc} values assume stoichiometric oxidation of Br⁻ by excess FAC. Uncertainties in the equilibrium constants of the brominating agents do not influence the fractional contributions to k_{calc} shown in this figure (section 10 of the Supporting Information for more details).

on k_{calc} (where $k_{calc} = k_{BrCl}[BrCl] + k_{Br_2}[Br_2] + k_{BrOCl}[BrOCl] + k_{Br_2O}[Br_2O] + k_{HOBr}[HOBr]$) for typical DW chlorination conditions are shown in part A of Figure 4. At pH < 7.1, BrCl is the predominant brominating agent; HOBr predominates at pH > 7.1. All other species contribute <20% throughout the entire pH 5−9 range. As shown in part B of Figure 4, the relative

importance of BrCl increases with increasing [Cl⁻]. Indeed, at pH 7 and [Cl⁻] typical of DW and WW treatment, BrCl is the predominant halogenating agent.

The effects of chlorine dose on k_{calc} are summarized in part C of Figure 4. At [FAC] typical of DW treatment, BrCl is the predominant oxidant. At higher [FAC], including those typical of some WW treatment scenarios, BrOCl becomes increasingly important because its concentration is proportional to the product [HOBr][HOCl] (eq 5). The influence of [Br⁻] on k_{calc} is shown in part D of Figure 4. At [Br⁻] representative of DW and WW treatment, BrCl is the predominant brominating agent. At higher [Br⁻], Br_2O contributes appreciably to k_{calc}. Although unlikely under most DW and WW treatment conditions, if [Br⁻]$_o$ > [FAC]$_o$, Br_2 may also play an important role (data not shown). Such conditions might be encountered, for example, in arid locations, in regions affected by seawater intrusion, and in desalination systems.[64] Moreover, in laboratory studies generating HOBr via ozonation of bromide, yields of ~95% have been reported.[65] In such solutions, Br_2 could potentially form via reactions of HOBr with any unoxidized bromide (eq 3). As Br_2 may be three or 4 orders of magnitude more reactive than HOBr (Table 2), the potential effects of Br_2 in such systems should not be dismissed.

Bromide concentration and pH are known to influence rates of DBP precursor bromination.[17,65] Our results highlight the importance of [FAC] and [Cl⁻] as two additional variables influencing bromination rates. As [BrOCl] is proportional to [HOCl] (at constant [HOBr]), the extent to which BrOCl influences overall rates of bromination will determine the sensitivity of these processes to chlorine dose. We previously demonstrated that chlorination rates of DM[18] and of three aromatic ethers[19] were subject to chloride catalysis via formation of Cl_2. The current work reveals that chloride can also serve as a potent catalyst of bromination via formation of BrCl. Chloride is commonly viewed as an inert constituent during water treatment operations. Yet our findings indicate that even modest increases in [Cl⁻] (e.g., due to coagulant dosing with $FeCl_3$) can increase rates of DM chlorination and bromination by factors of 3 and 9, respectively, at pH 7 (Figure 5). Even greater rate enhancements are anticipated at pH <7.
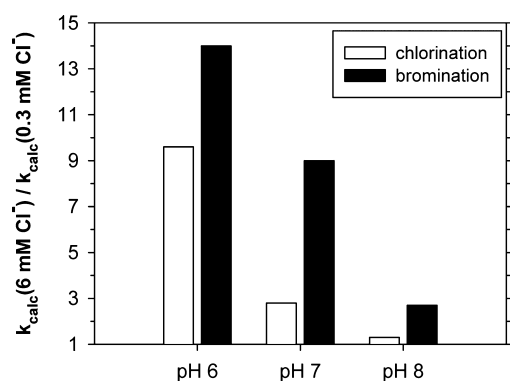

Figure 5. Chloride catalyzes the rates of DM chlorination *and* bromination. Calculated rate constants (k_{calc}) are shown at [Cl⁻] = 6 mM = 0.2 g/L (e.g., from addition of 2 mM $FeCl_3$ as a coagulant) relative to [Cl⁻] = 0.3 mM = 11 mg/L (the median chloride concentration of DW sources reported in ref 56) for DM chlorination and bromination at pH 6, 7, and 8. For chlorination, $k_{calc} = k_{Cl_2O}[Cl_2O] + k_{Cl_2}[Cl_2] + k_{HOCl}[HOCl]$ (ref 18). For bromination, $k_{calc} = k_{BrCl}[BrCl] + k_{BrOCl}[BrOCl] + k_{Br_2O}[Br_2O] + k_{HOBr}[HOBr]$. Values of rate constants are listed in Table 2. Other conditions: $T = 20 °C$, [FAC]$_o$ = 28 μM = 2 mg/L as Cl_2, and [Br⁻] = 1.25 μM = 100 μg/L (bromination case only).

Our findings challenge the conventional wisdom that assumes HOBr and OBr⁻ are the only species contributing to bromination reactions during water disinfection and laboratory investigations thereof. Indeed, very few reports in the environmental literature[9,10] have attempted to delineate the reactivities of brominating agents other than HOBr or OBr⁻ in solutions of FAC and Br⁻. The influence of the more reactive (but less abundant) brominating agents (BrCl, Br_2, BrOCl, and Br_2O) is anticipated to decrease for aromatic compounds possessing greater nucleophilicity than the model aromatic compound examined herein. Indeed, a similar trend was previously observed[19] for the chlorinating agents Cl_2, Cl_2O, and HOCl when their reactivity toward three aromatic ethers was assessed: as the nucleophilicity of the aromatic ethers increased, the relative importance of the more reactive (but less abundant) chlorinating agents Cl_2 and Cl_2O decreased relative to the less reactive (but more abundant) HOCl. Further studies are needed to determine whether BrCl, BrOCl, Br_2O, and Br_2 influence bromination rates of other organic compounds, including precursors of regulated DBPs, under conditions encountered during water treatment.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Reagents, method details, data modeling, and additional experimental results. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 410-516-4387; Fax: 410-516-8996; E-mail: lroberts@jhu.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Cowman, G. A.; Singer, P. C. Effects of bromide ion on haloacetic acid speciation resulting form chlorination and chloramination of aquatic humic substances. *Environ. Sci. Technol.* **1996**, *30*, 16−24.

(2) Hua, G.; Reckhow, D. A.; Kim, J. Effect of bromide and iodide ions on the formation and speciation of disinfection byproducts during chlorination. *Environ. Sci. Technol.* **2006**, *40*, 3050−3056.

(3) Sun, Y.; Wu, Q.; Hu, H.; Tian, J. Effect of bromide on the formation of disinfection by-products during wastewater chlorination. *Water Res.* **2009**, *43*, 2391−2398.

(4) Richardson, S. D.; Plewa, M. J.; Wagner, E. D.; Schoeny, R.; DeMarini, D. M. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. *Mutat. Res.* **2007**, *636*, 178−242.

(5) Kumar, K.; Margerum, D. W. Kinetics and mechanism of general-acid-assisted oxidation of bromide by hypochlorite and hypochlorous acid. *Inorg. Chem.* **1987**, *26*, 2706−2711.

(6) Eigen, M.; Kustin, K. The kinetics of halogen hydrolysis. *J. Am. Chem. Soc.* **1962**, *84*, 1355−1361.

(7) Liu, Q.; Margerum, D. W. Equilibrium and kinetics of bromine chloride hydrolysis. *Environ. Sci. Technol.* **2001**, *35*, 1127−1133.

(8) Liebhafsky, H. A. The equilibrium constant of the bromine hydrolysis and its variation with temperature. *J. Am. Chem. Soc.* **1934**, *56*, 1500−1505.

(9) Voudrias, E. A.; Reinhard, M. Reactivities of hypochlorous and hypobromous acid, chlorine monoxide, hypobromous acidium ion, chlorine, bromine, and bromine chloride in electrophilic aromatic substitution reactions with *p*-xylene in water. *Environ. Sci. Technol.* **1988**, *22*, 1049−1056.

(10) Voudrias, E. A.; Reinhard, M. A kinetic model for the halogenation of p-xylene in aqueous HOCl solutions containing Cl⁻ and Br⁻. *Environ. Sci. Technol.* **1988**, *22*, 1056−1062.

(11) Margerum, D. W.; Huff Hartz, K. E. Role of halogen(I) cation-transfer mechanisms in water chlorination in the presence of bromide ion. *J. Environ. Monitor.* **2002**, *4*, 20−26.

(12) Orlando, J. J.; Burkholder, J. B. Gas-phase UV/visible absorption spectra of HOBr and Br$_2$O. *J. Phys. Chem.* **1995**, *99*, 1143−1150.

(13) Deters, B.; Burrows, J. P.; Himmelmann, S.; Blindauer, C. Gas phase spectra of HOBr and Br$_2$O and their atmospheric significance. *Ann. Geophys.* **1996**, *14*, 468−475.

(14) Burkholder, J. B.; Knight, G.; Orlando, J. J. UV absorption spectrum of BrOCl. *J. Photoch. Photobiol. A* **2000**, *134*, 133−137.

(15) Aguzzi, A.; Rossi, M. J. Heterogeneous hydrolysis and reaction of BrONO$_2$ and Br$_2$O on pure ice and ice doped with HBr. *J. Phys. Chem. A* **2002**, *106*, 5891−5901.

(16) Iraci, L. T.; Michelsen, R. R.; Ashbourn, S. F. M.; Rammer, T. A.; Golden, D. M. Uptake of hypobromous acid (HOBr) by aqueous sulfuric acid solutions: Low-temperature solubility and reaction. *Atmos. Chem. Phys.* **2005**, *5*, 1577−1587.

(17) Lee, Y.; von Gunten, U. Transformation of 17α-ethinylestradiol during water chlorination: Effects of bromide on kinetics, products, and transformation pathways. *Environ. Sci. Technol.* **2009**, *43*, 480−487.

(18) Sivey, J. D.; McCullough, C. E.; Roberts, A. L. Chlorine monoxide (Cl$_2$O) and molecular chlorine (Cl$_2$) as active chlorinating agents in reaction of dimethenamid with aqueous free chlorine. *Environ. Sci. Technol.* **2010**, *44*, 3357−3362.

(19) Sivey, J. D.; Roberts, A. L. Assessing the reactivity of free chlorine constituents Cl$_2$, Cl$_2$O, and HOCl toward aromatic ethers. *Environ. Sci. Technol.* **2012**, *46*, 2141−2147.

(20) Gianessi, L.; Reigner, N. Pesticide use in U.S. crop production: 2002. http://www.croplifefoundation.org/Documents/PUD/NPUD%202002/Fung%20&%20Herb%202002%20Data%20Report.pdf (Aug 31, 2012).

(21) Hladik, M. L.; Bouwer, E. J.; Roberts, A. L. Neutral chloroacetamide herbicide degradates and related compounds in Midwestern United States drinking water sources. *Sci. Total Environ.* **2008**, *390*, 155−165.

(22) Hladik, M. L.; Bouwer, E. J.; Roberts, A. L. Neutral degradates of chloroacetamide herbicides: Occurrence in drinking water and removal during conventional water treatment. *Water Res.* **2008**, *42*, 4905−4914.

(23) Hladik, M. L.; Roberts, A. L.; Bouwer, E. J. Removal of neutral chloroacetamide herbicide degradates during simulated unit processes for drinking water treatment. *Water Res.* **2005**, *39*, 5033−5044.

(24) Acero, J. L.; Piriou, P.; von Gunten, U. Kinetics and mechanisms of formation of bromophenols during drinking water chlorination: Assessment of taste and odor development. *Water Res.* **2005**, *39*, 2979−2993.

(25) Roth, W. A. Zur Thermochemie des Chlors und der unterchlorigen Säure. *Z. Phys. Chem. Abt. A* **1929**, *145*, 289−297.

(26) Denis, P. A. Thermochemistry of the hypobromous and hypochlorous acids, HOBr and HOCl. *J. Phys. Chem. A* **2006**, *110*, 5887−5892.

(27) Karton, A.; Parthiban, S.; Martin, J. M. L. Post-CCSD(T) ab initio thermochemistry of halogen oxides and related hydrides XOX, XOOX, HOX, XO$_n$, and HXO$_n$ (X = F, Cl), and evaluation of DFT methods for these systems. *J. Phys. Chem. A* **2009**, *113*, 4802−4816.

(28) Grant, D. J.; Garner, E. B., III; Matus, M. H.; Nguyen, M. T.; Peterson, K. A.; Francisco, J. S.; Dixon, D. A. Thermodynamic properties of the XO$_2$, X$_2$O, XYO, X$_2$O$_2$, and XYO$_2$ (X, Y = Cl, Br and I) isomers. *J. Phys. Chem. A* **2010**, *114*, 4254−4265.

(29) Feller, D.; Peterson, K. A.; de Jong, W. A.; Dixon, D. A. Performance of coupled cluster theory in thermochemical calculations of small halogenated compounds. *J. Chem. Phys.* **2003**, *118*, 3510−3522.

(30) Karton, A.; Taylor, P. R.; Martin, J. M. L. Basis set convergence of post-CCSD contributions to molecular atomization energies. *J. Chem. Phys.* **2007**, *127*, 064104.

(31) Tew, D. P.; Klopper, W.; Heckert, M.; Gauss, J. Basis set limit CCSD(T) harmonic vibrational frequencies. *J. Phys. Chem.* **2007**, *111*, 11242−11248.

(32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J., A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.

(33) Stanton, J. F.; Gauss, J.; Harding, M. E.; Szalay, P. G.; Auer, A. A.; Bartlett, R. J.; Benedikt, U.; Berger, C.; Bernholdt, D. E.; Bomble, Y. J.; Cheng, L.; Christiansen, O.; Heckert, M.; Heun, O.; Huber, C.; Jagau, T.-C.; Jonsson, D.; Jusélius, J.; Klein, K.; Lauderdale, W. J.; Matthews, D. A.; Metzroth, T.; O'Neill, D. P.; Price, D. R.; Prochnow, E.; Ruud, K.; Schiffmann, F.; Schwalbach, W.; Stopkowicz, S.; Tajti, A.; Vázquez, J.; Wang, F.; Watts, J. D.; Almlöf, J.; Taylor, P. R.; Helgaker, T.; Jensen, H. J. A.; Jørgensen, P.; Olsen, J.; Mitin, A. V.; van Wüllen, C. *CFOUR, Coupled-Cluster Techniques for Computational Chemistry: A Quantum-Chemical Program Package with integral packages MOLECULE, PROPS, ABACUS, and ECP routines, 1* **2010**.

(34) Kállay, M.; Surján, P. R. Higher excitations in coupled-cluster theory. *J. Chem. Phys.* **2001**, *115*, 2945.

(35) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. Quadratic configuration interaction - a general technique for determining electron correlation energies. *J. Chem. Phys.* **1987**, *87*, 5968−5975.

(36) Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007−1023.

(37) Woon, D. E.; Dunning, T. H. Gaussian-basis sets for use in correlated molecular calculations. 3. The atoms aluminum through argon. *J. Chem. Phys.* **1993**, *98*, 1358−1371.

(38) Wilson, A. K.; Woon, D. E.; Peterson, K. A.; Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. IX. The atoms Gallium through Krypton. *J. Chem. Phys.* **1999**, *110*, 7667−7676.

(39) Boese, D. A.; Martin, J. M. L.; Klopper, W. Basis set limit coupled cluster study of H-bonded systems and assessment of more approximate methods. *J. Phys. Chem. A* **2007**, *111*, 11122−11133.

(40) Halkier, A.; Klopper, W.; Helgaker, T.; Jorgensen, P. Basis-set convergence of the molecular electric dipole moment. *J. Chem. Phys.* **1999**, *111*, 4424−4430.

(41) Noga, J.; Bartlett, R. J. The full CCSDT model for molecular electronic structure. *J. Chem. Phys.* **1987**, *86*, 7041.

(42) Noga, J.; Bartlett, R. J. Erratum: The full CCSDT model for molecular electronic structure [J. Chem. Phys. 86, 7041 (1987)]. *J. Chem. Phys.* **1988**, *89*, 3401.

(43) Bomble, Y. J.; Kallay, M.; Gauss, J.; Stanton, J. F. Coupled cluster methods including noniterative approximate quadruple excitation corrections. *J. Chem. Phys.* **2005**, *123*, 054101.

(44) Oliphant, N.; Adamowicz, L. Coupled-cluster method truncated at quadruples. *J. Chem. Phys.* **1991**, *95*, 6645.

(45) Schwenke, D. W. The extrapolation of one-electron basis sets in electronic structure calculations: How it should work and how it can be made to work. *J. Chem. Phys.* **2005**, *122*, 014107.

(46) Peterson, K. A.; Dunning, T. H. Accurate correlation consistent basis sets for molecular core—valence correlation effects: The second row atoms Al—Ar, and the first row atoms B—Ne revisited. *J. Chem. Phys.* **2002**, *117*, 10548—10560.

(47) DeYonker, N. J.; Peterson, K. A.; Wilson, A. K. Systematically convergent correlation consistent basis sets for molecular core-valence correlation effects: The third-row atoms Gallium through Krypton. *J. Chem. Phys. A* **2007**, *111*, 11383—11393.

(48) Douglas, M.; Kroll, N. M. Quantum electrodynamical corrections to fine-structure of helium. *Ann. Phys. (NY)* **1974**, *82*, 89—155.

(49) Jansen, G.; Hess, B. A. Revision of the Douglas-Kroll transformation. *Phys. Rev. A* **1989**, *39*, 6016—6017.

(50) de Jong, W. A.; Harrison, R. J.; Dixon, D. A. Parallel Douglas—Kroll energy and gradients in NWChem: Estimating scalar relativistic effects using Douglas—Kroll contracted basis sets. *J. Chem. Phys.* **2001**, *114*, 48—53.

(51) Bryantsev, V. S.; Diallo, M. S.; Goddard, W. A. Calculation of solvation free energies of charged solutes using mixed cluster/continuum models. *J. Phys. Chem. B* **2008**, *112*, 9709—9719.

(52) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989; p 271.

(53) Ennis, C. A.; Birks, J. W. Applications of a new laboratory source of gaseous HOCl: Product distribution in the Cl + HOCl reaction and equilibrium constant for the reaction $Cl_2O + H_2O = 2HOCl$. *J. Phys. Chem.* **1985**, *89*, 186—191.

(54) Reinhard, M.; Redden, G. D.; Voudrias, E. A. The hydrolysis constant of chlorine monoxide and bromine chloride in water. In *Water Chlorination: Environmental Impact and Health Effects*, Jolley, R. L., et al., Ed.; Ann Arbor Science: Ann Arbor, MI, 1990; pp 859—870.

(55) Westerhoff, P.; Siddiqui, M.; Debroux, J.; Zhai, W.; Ozekin, K.; Amy, G. Nation-wide bromide occurrence and bromate formation potential in drinking water supplies. In *Critical Issues in Water and Wastewater Treatment: Proceedings of the 1994 National Conference on Environmental Engineering*; Ryan, J. N., Edwards, M., Eds. American Society of Civil Engineers: New York, 1994; pp 670—677.

(56) Davis, S. N.; DeWiest, R. J. M. *Hydrogeology*; Wiley: New York, 1966; p 463.

(57) Swain, C. G.; Crist, D. R. Mechanisms of chlorination by hypochlorous acid. The last of chlorinium ion, Cl^+. *J. Am. Chem. Soc.* **1972**, *94*, 3195—3200.

(58) Snider, E. H.; Alley, F. C. Kinetics of the chlorination of biphenyl under conditions of waste treatment processes. *Environ. Sci. Technol.* **1979**, *13*, 1244—1248.

(59) Ichihashi, K.; Teranishi, K.; Ichimura, A. Brominated-trihalomethane formation from phenolic derivatives as a model of humic materials by the reaction with hypochlorite and hypobromite ions. *Chem. Lett.* **1999**, *9*, 957—958.

(60) Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*; University Science: Sausalito, CA, 2005; p 1104.

(61) Darwent, B. d. *Bond Dissociation Energies of Simple Molecules*; National Standard Reference Data System: Washington DC, 1970.

(62) Tchobanoglous, G.; Burton, F. L.; Stensel, H. D. *Wastewater Engineering: Treatment and Reuse*; McGraw-Hill: Boston, 2003; p 1819.

(63) Crittenden, J.; Trussell, R.; Hand, D.; Howe, K.; Tchobanoglous, G. *Water Treatment Principles and Design*; John Wiley: Hoboken, NJ, 2005; p 1948.

(64) Agus, E.; Voutchkov, N.; Sedlak, D. L. Disinfection by-products and their potential impact on the quality of water produced by desalination systems: A literature review. *Desalination* **2009**, *237*, 214—237.

(65) Gallard, H.; Pellizzari, F.; Croue, J. P.; Legube, B. Rate constants of reactions of bromine with phenols in aqueous solution. *Water Res.* **2003**, *37*, 2883—2892.