

# Equilibria and Speciation of Chloramines, Bromamines, and Bromochloramines in Water

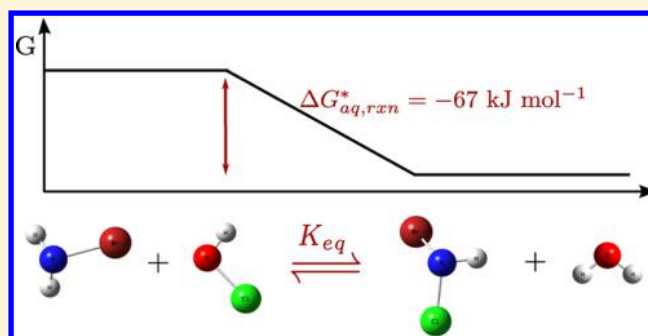
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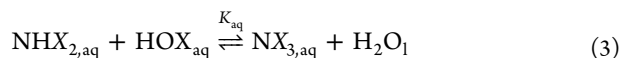
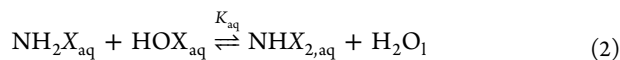
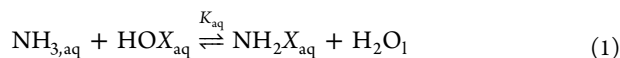
**S** Supporting Information

**ABSTRACT:** The stabilities and speciation of the halamines in water are difficult to characterize experimentally. We provide theoretical estimates of aqueous standard free energies of formation for inorganic chloramines, bromamines, and bromochloramines, based on high-accuracy theoretical standard free energies of formation in gas phase combined with quantum chemical estimates of Henry's law constant. Based on comparisons between several theoretical and experimental datasets, we assign an error of 1.1–1.2 log unit for equilibrium constants of several reactions leading to halamines in water. The reactions of ammonia with HOCl or HOBr that lead to dichloramine, trichloramine, and tribromamine are found to be thermodynamically more favorable than was previously believed. The newly reported equilibrium data also allow us to propose rate constant values for some hydrolysis and disproportionation reactions of dichloramine, monobromamine, and bromochloramine. Finally, theoretical results indicate aqueous acid dissociation constant ( $pK_a$ ) values of  $1.5 \pm 1$  for  $\text{NH}_3\text{Cl}^+$ ,  $0.8 \pm 1$  for  $\text{NH}_3\text{Br}^+$ ,  $11.8 \pm 1$  for  $\text{NHCl}_2$ , and  $12.5 \pm 1$  for  $\text{NHBrCl}$ . The present report provides a comprehensive data set describing the free energies of the neutral inorganic halamines, the anionic conjugate base species, and the cationic conjugate acid species, with approximately uniform uncertainty bounds assigned throughout.



## INTRODUCTION

Aqueous chloramines, bromamines, and bromochloramines, collectively termed halamines in the present work, typically arise from the *N*-substitution reactions of hypohalous acids with ammonia:<sup>1–16</sup>



where *X* is either Cl or Br. Dichloramine,<sup>5,6,17,18</sup> dibromamine,<sup>8,14,19</sup> and bromochloramine<sup>20</sup> can also form by disproportionation reactions. Chloramines are applied widely as disinfectants in water treatment facilities, and their decomposition is directly implicated in the production of potentially toxic disinfection byproducts (DBPs).<sup>21–44</sup> During chloramination of natural waters, chloramines can provide the nitrogen source for the formation of several families of nitrogenous disinfection byproducts, including halonitriles,<sup>32,37</sup> halonitroalkanes,<sup>32,37</sup> and nitrosamines.<sup>32,33,38–45</sup> Chloramines can also participate in substitution and redox reactions with organic micropollutants.<sup>31,40,41,45–47</sup>

The presence of naturally occurring bromide in fresh waters can potentially lead to the production of hypobromous acid, bromamines, and bromochloramines, during chlorination, chloramination, or ozonation of natural waters.<sup>8,10,12,15,19,20,44,48–53</sup> During oxidative treatment of natural water, bromide can react with hypochlorous acid to produce HOBr,<sup>54,55</sup> which can subsequently brominate ammonia and substituted amines, thereby producing bromamines (eqs 1–3). These species can then further react rapidly to form dibromamine, tribromamine, and bromochloramines (eqs 1–3).<sup>19,20,51,52,56,57</sup> Bromamines and bromochloramines can lead to the production of potentially toxic DBPs in water as well.<sup>58–61</sup> For example,  $\text{NHBr}_2$  and  $\text{NHBrCl}$  are thought to be involved in the production of NDMA<sup>59,60</sup> and of CNBr<sup>58,61</sup> during water disinfection.

Chloramines and bromamines also arise in activated neutrophil and eosinophil cells during inflammatory disease affecting mammals, due to the reactions of HOCl or HOBr with nitrogen-containing biological molecules such as proteins and amino acids.<sup>62,63</sup> Thus, formed bromamines and chloramines can undergo oxidation reactions with  $\text{O}_2$ <sup>–63</sup> or metal ions,<sup>64,65</sup>

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generating nitrogen- and carbon-centered radicals. The spontaneous decomposition of such radical intermediates can damage the cell, inducing protein fragmentation, protein modification, and tissue damage.<sup>64,65</sup>

Despite that the halamines have been studied for several decades, chemical equilibrium constants remain highly uncertain for relevant formation, disproportionation, and protonation/deprotonation reactions of many of these species. The rate constants and the equilibrium constants of the reactions involving chloramines are difficult to measure because several short-lived species can arise simultaneously, and in many cases these values must be constrained with kinetic models.<sup>1,3,9,13,18,20,66,67</sup> The equilibria and the kinetics describing the production of bromamines and mixed halamines are also incomplete.<sup>11,19,49,51,68,69</sup> Further complicating matters, the acid dissociation constant ( $pK_a$ ) values remain unknown for most of the neutral chloramines, bromamines, and bromochloramines and also for their cationic conjugate acids.<sup>4,70</sup>

Quantum chemical models provide an alternative approach for the determination of the aqueous equilibria of halamines. For example, chlorination reactions of amino functional groups were studied recently by computational chemical approaches.<sup>71–74</sup> Rayson et al.<sup>72</sup> and Andrés et al.<sup>71</sup> investigated the oxidation of ammonia with HOCl by employing density functional methods. In other work, the G3B3<sup>75</sup> composite method was used to describe *N*-chlorination reactions of organic amines by HOCl.<sup>73</sup> Theoretical methods were also used by Rayne and Forest to estimate aqueous free energies of reactions leading to chloramines (eqs 1–3).<sup>74</sup> However, these approaches do not achieve sub-kcal mol<sup>-1</sup> accuracy in the free energies of the aqueous reactions leading to chloramines. For example, the gas phase theoretical enthalpies of reaction of Rayne and Forest exhibit discrepancies with respect to more accurate benchmark data published recently.<sup>76,77</sup> Standard heats of formation ( $\Delta H_f^\circ$ ) and standard free energies of formation ( $\Delta G_f^\circ$ ) in gas phase were determined recently using high-accuracy theoretical methods for chloramines, bromamines, and bromochloramines, and these data were assigned uncertainties of 1–3 kJ mol<sup>-1</sup>.<sup>76,77</sup> However, the influence of aqueous solvent on these gas phase thermodynamic data remains to be established.

The goal of the present study is to establish reliable estimates of the standard free energies of formation and the acid dissociation constants of inorganic chloramines, bromamines, and bromochloramines in aqueous solution. We compare these theoretical results with available experimental data. Attention is paid to reporting realistic uncertainty bounds for these theoretically estimated thermodynamic properties. The results enable us to determine the aqueous equilibria for the principal pathways that generate halamines during drinking water treatment.

## MATERIALS AND METHODS

**Computational Estimates of Free Energies of Solvation.** The free energy of aqueous solvation of a chemical species,  $\Delta G_{\text{solv}}^*$ , describes its equilibrium distribution between the gas and aqueous phases. According to the standard state convention used in the present study,  $\Delta G_{\text{solv}}^*$  is defined as the energy required to transfer one mole of a chemical species from the gas phase to aqueous solution at a (hypothetically infinitely dilute) 1 M concentration in both phases.<sup>78</sup> The free energy of aqueous solvation is related to the experimentally measurable dimensionless Henry's law solubility constant,  $K_H^{(-)}$ :

$$\Delta G_{\text{solv}}^* = RT \ln K_H^{(-)} \quad (4)$$

More details on the conversion factors and the units of the Henry's law constant values are provided in the SI. To estimate  $\Delta G_{\text{solv}}^*$  values of the halamines, we considered several methodological approaches, including four implicit solvent models and also a cluster-continuum approach adapted from the method of Bryantsev and co-workers.<sup>79</sup>

**Implicit Solvent Models: Methods and Basis Sets.** Gas phase geometries for the halamines, HOCl, HOBr, NH<sub>3</sub>, and H<sub>2</sub>O were computed with the CCSD(T) electronic structure method and were taken from recent high-accuracy theoretical results.<sup>76,77</sup> The gas phase geometries of Cl<sub>2</sub>, Br<sub>2</sub>, and NF<sub>3</sub> were optimized using the B2PLYPD<sup>80,81</sup> DFT method with the aug-cc-pVQZ basis set,<sup>82–84</sup> as implemented in Gaussian09.<sup>85</sup> Harmonic frequency analyses were subsequently carried out with the same electronic structure method used to obtain the geometries.

The implicit solvent models employed were the universal solvent model based on the solute electron density<sup>86</sup> (SMD), the polarizable conductor calculation model (CPCM),<sup>87,88</sup> and the polarizable conductor model (PCM)<sup>88–91</sup> as implemented in Gaussian09,<sup>85</sup> and the conductor-like screening model (COSMO)<sup>92,93</sup> implemented in NWChem.<sup>94</sup> Free energies of solvation computed with these models are referred to as  $\Delta G_{\text{solv,SMD}}^*$ ,  $\Delta G_{\text{solv,CPCM}}^*$ ,  $\Delta G_{\text{solv,PCM}}^*$ , and  $\Delta G_{\text{solv,COSMO}}^*$ , respectively.

To obtain  $\Delta G_{\text{solv,SMD}}^*$ ,  $\Delta G_{\text{solv,CPCM}}^*$ ,  $\Delta G_{\text{solv,PCM}}^*$ , and  $\Delta G_{\text{solv,COSMO}}^*$  for the species studied here, we performed B2PLYPD/aug-cc-pVQZ single point energy computations with the implicit solvent models SMD, CPCM, PCM, and COSMO, using the gas phase optimized geometries. The B2PLYPD method has been reported to give good performance for challenging multireference electronic structures such as halogen oxides.<sup>95–98</sup> To briefly test whether B2PLYPD is appropriate for the electronic structures of halamines and other halogen oxidants studied here, we evaluated gas phase total atomization energies and compared these results to recently published<sup>76,77</sup> benchmark values (Table S2 in the Supporting Information (SI)). Based on the good performance of the B2PLYPD method for gas phase electronic structure predictions, we carried out free energy of solvation computations with B2PLYPD. Computations with the CPCM and PCM implicit solvent models were tried with different atomic radii (UFF, UAHF, and UAKS) as implemented in Gaussian09. To consistently calculate the solvent effect with the B2PLYPD method, we included the keyword SCRF(*ExternalIteration*)<sup>99,100</sup> in the Gaussian09 input.

**Cluster-Continuum Solvent Models: Methods and Basis Sets.** The cluster-continuum approach may allow a more accurate description of aqueous solvation effects, by including an explicit electronic treatment of interactions with one or more molecules of water.<sup>79</sup> Compared to implicit models, this approach has been found to give improved results for monatomic ions.<sup>79</sup> The cluster-continuum approach has also been applied for neutral and charged organic molecules.<sup>95</sup> We obtained cluster-continuum results in combination with both the SMD and COSMO implicit solvent models. To apply this method, we employ a microsolvated cluster that contains the molecule of interest and one explicitly modeled molecule of water, together embedded in a conventional implicit solvent model. For the neutral halamine species studied here, a stable binary complex can be made between the halamine molecule

**Table 1. Gibbs Free Energies of Solvation for Cl<sub>2</sub>, Br<sub>2</sub>, NF<sub>3</sub>, NH<sub>3</sub>, H<sub>2</sub>O, HOCl, Inorganic Chloramines, and Methylated Amines: Experimental Values and Theoretical Estimates. Values are in kJ mol<sup>-1</sup>**

compounds	$\Delta G_{\text{sol},\text{Expt}}^*$	$\Delta G_{\text{sol},\text{SMD}}^*$	$\Delta G_{\text{sol},\text{cluster-SMD}}^*$	$\Delta G_{\text{sol},\text{half-and-half}}^*$
Set A				
Cl <sub>2</sub>	-2.0 <sup>a</sup> ± 0.7	2.0	4.5	3.2
Br <sub>2</sub>	-7.1 <sup>a</sup> ± 0.7	-4.4	-3.7	-4.1
NF <sub>3</sub>	9.8 <sup>a</sup> ± 0.7	10.8	14.1	12.4
H <sub>2</sub> O	-26.4 <sup>b</sup>	-28.6	-25.9	-27.3
NH <sub>3</sub>	-18.1 <sup>a</sup> ± 1.3	-13.1	-19.7	-16.4
NH <sub>2</sub> CH <sub>3</sub>	-19.1 <sup>c</sup> ± 2.5	-15.2	-16.3	-15.8
NH(CH <sub>3</sub> ) <sub>2</sub>	-17.9 <sup>c</sup> ± 2.5	-15.2	-13.7	-14.5
Set B				
NH <sub>2</sub> Cl	-19.0 <sup>a</sup> ± 4.2	-16.3	-15.7	-16.0
NHCl <sub>2</sub>	-16.3 <sup>a</sup> ± 4.2	-10.2	-7.5	-8.8
NCl <sub>3</sub>	-2.2 <sup>a</sup> ± 4.2	2.6	-3.6	-0.5
HOCl	-24.0 <sup>a</sup> ± 4.2	-16.7	-21.8	-19.2
Set A				
root mean square error		3.3	3.8	3.2
maximum signed deviation		5.0 (NH <sub>3</sub> )	6.5 (Cl <sub>2</sub> )	5.3 (Cl <sub>2</sub> )
Set B				
root mean square error		5.5	4.9	4.8
maximum signed deviation		7.3 (HOCl)	8.8 (NHCl <sub>2</sub> )	7.5 (NHCl <sub>2</sub> )

<sup>a</sup>Experimental free energies of solvation, based on Henry's law constant values, are taken from Sander's compilation.<sup>124</sup> <sup>b</sup>The experimental free energy of solvation of H<sub>2</sub>O is taken from Marenich et al.<sup>125</sup> <sup>c</sup>Estimates of Henry's law constant values were taken from Sander's compilation.<sup>126</sup>

and a single water molecule, in all cases by way of a hydrogen bond between the water H atom and the halamine N atom. Natural population analysis indicates that the N atom has a partial negative charge in all nine inorganic chloramine, bromamine, and bromochloramine structures,<sup>101</sup> which facilitates this H-bond interaction with nearby aqueous solvent. Our cluster-continuum results assume that this hydrogen-bonded structure is representative of the interaction between a halamine solute and a nearby water molecule in aqueous solvent. We did not see an advantage in increasing the number of explicit water molecules within the cluster-continuum framework. In our trial computations with a test set of neutral halogenated molecules including halamines, clusters containing the solute plus two explicitly modeled water molecules often exhibited shallow potential energy basins, and these clusters typically could occupy multiple stable geometric configurations that differed little in the potential energy (results not shown). We concluded that solvated clusters containing multiple water molecules were not suited to the cluster-continuum approach. The cluster-continuum model assumes that the geometric configuration of the cluster represents the most typical solvent structure near the solute, and the model also assumes that this configuration occupies a well-defined potential energy basin. The cluster-continuum estimate of the free energy of solvation can be obtained by an appropriate thermodynamic cycle,<sup>79</sup> explained further in the SI. The free energies of solvation computed with the cluster-continuum approaches are referred to as  $\Delta G_{\text{sol},\text{cluster-SMD}}^*$  and  $\Delta G_{\text{sol},\text{cluster-COSMO}}^*$ , depending on the implicit model used with the cluster.

To obtain free energies of solvation computed with the cluster-continuum approaches,  $\Delta G_{\text{sol},\text{cluster-SMD}}^*$  and  $\Delta G_{\text{sol},\text{cluster-COSMO}}^*$ , it was necessary to compute several quantities, as shown in eqs S4 and S5 in the SI. We conducted a gas phase geometry optimization of a cluster of the solute and one explicit molecule of water with the B2PLYPD/aug-cc-pVQZ model chemistry for chloramines, bromamines, bromochloramines, NH<sub>3</sub>, H<sub>2</sub>O, HOCl, HOBr, Cl<sub>2</sub>, Br<sub>2</sub>, and

NF<sub>3</sub>. In order to solve consistently the thermodynamic cycle on which the cluster-continuum approach is based, we performed additional gas phase geometry optimizations with B2PLYPD/aug-cc-pVQZ for all species. Harmonic vibrational frequency analyses were performed with B2PLYPD/aug-cc-pVQZ, used to compute gas phase thermal contributions to the free energies and to confirm the nature of the stationary points on the B2PLYPD potential energy surface. To evaluate the term in SI eq S4,  $\Delta G_{\text{sol},\text{SMD}}^*(X(\text{H}_2\text{O}))$  that is used in the cluster-continuum-SMD approach (and the analogous term in the cluster-continuum-COSMO approach), we also carried out single point energy computations with SMD and COSMO implicit solvent models on gas phase geometries of a cluster of the solute and one explicit molecule of water.

**Computational Estimates of Aqueous pK<sub>a</sub>.** We estimated aqueous acidity constant (pK<sub>a</sub>) values for the deprotonation of both the neutral species and the cationic conjugate acid ammonium species, for several halamines. It is difficult to estimate absolute pK<sub>a</sub> values a priori with theoretical methods.<sup>102–104</sup> Therefore, we took advantage of the linear free energy relationship (LFER) that is commonly found between experimental and theoretical pK<sub>a</sub> values within a family of structurally related acids.<sup>95,102,105–107</sup> We computed uncorrected quantum chemical acidity constant values according to the equation:

$$\text{p}K_a^{\text{uncorrected}} = \frac{\Delta G_{\text{aq}}^{\text{dep,uncorrected}}}{2.303RT} \quad (5)$$

where  $\Delta G_{\text{aq}}^{\text{dep,uncorrected}}$  is the raw quantum chemical estimate of the free energy of the aqueous deprotonation reaction. To obtain  $\Delta G_{\text{aq}}^{\text{dep,uncorrected}}$ , gas phase geometry optimizations, harmonic vibrational frequency analyses, and single point energy computations were conducted with the CBS-QB3<sup>108,109</sup> composite method. The CBS-QB3 method has previously been shown to give good results for the proton affinities used in pK<sub>a</sub> predictions.<sup>95,110–113</sup> Solvation free energies were computed with the SMD implicit solvent

**Table 2. Theoretical Standard Free Energies of Formation in Gas Phase ( $\Delta_f G_{\text{gas,Comp}}^\circ$ ), Theoretical Free Energies of Aqueous Solvation ( $\Delta G_{\text{solv,half-and-half}}^*$ ), and Theoretical and Experimental Aqueous Standard Free Energies of formation ( $\Delta_f G_{\text{aq}}^*$ ) for Halamines and Related Compounds. Values are in  $\text{kJ mol}^{-1}$**

compounds	$\Delta_f G_{\text{gas,Comp}}^\circ$ <sup>a</sup>	$\Delta G_{\text{solv,half-and-half}}^*$ <sup>b</sup>	$\Delta_f G_{\text{aq,Comp}}^*$ <sup>b</sup>	$\Delta_f G_{\text{aq,Expt}}^*$
NH <sub>2</sub> Cl	81.1 ± 1	-16.0 ± 6	73.1 ± 6	66.9 <sup>c</sup> , 84.0 ± 0.4 <sup>d</sup>
NHCl <sub>2</sub>	174.1 ± 1	-8.8 ± 6	173.3 ± 6	176.6 <sup>c</sup> , 209.2 ± 1.2 <sup>d</sup>
NCl <sub>3</sub>	267.1 ± 1	-0.5 ± 6	274.5 ± 6	299.2 <sup>c</sup> , 341.4 ± 1.8 <sup>d</sup>
NH <sub>2</sub> Br	96.2 ± 1	-14.9 ± 6	89.1 ± 6	77.0 <sup>c</sup> , 84.3 ± 0.5 <sup>d</sup>
NHBr <sub>2</sub>	206.9 ± 3	-9.4 ± 6	205.5 ± 7	181.1 <sup>c</sup> , 203.2 ± 1.5 <sup>d</sup>
NBr <sub>3</sub>	306.1 ± 3	0.4 ± 6	314.4 <sup>e</sup> ± 7	295.8 <sup>c</sup> , 329.6 ± 2.5 <sup>d</sup>
NHBrCl	184.9 ± 3	-8.8 ± 6	184.0 ± 7	
NBrCl <sub>2</sub>	282.7 ± 3	2.9 ± 6	293.5 <sup>e</sup> ± 7	
NBr <sub>2</sub> Cl	292.9 ± 3	0.3 ± 6	301.2 ± 7	
NH <sub>3</sub>	-15.8 ± 1	-16.4 ± 6	-24.3 ± 6	-26.6 <sup>c</sup>
H <sub>2</sub> O	-228.9 ± 1	-17.3 ± 6 <sup>f</sup>	-238.3 ± 6 <sup>f</sup>	-237.2 <sup>g</sup>
HOCl	-64.8 ± 1	-19.2 ± 6	-76.1 ± 6	-79.9 <sup>c</sup>
HOBr	-63.4 ± 1	-16.2 ± 6	-71.7 ± 6	-82.4 <sup>c</sup>

<sup>a</sup>The gas phase standard free energies of formation at 298 K were taken from previous high-accuracy theoretical data.<sup>76,77</sup> <sup>b</sup>The error intervals reported for the theoretical standard free energy values are interpreted as error bounds that are expected to contain 95% of the deviations. <sup>c</sup>These experimental aqueous standard free energies of formation were taken from Sugam and Helz.<sup>69</sup> No uncertainty bounds are available. <sup>d</sup>These experimental aqueous standard free energies of formation were taken from Soulard and co-workers.<sup>12</sup> <sup>e</sup>Exceptionally, the cluster-continuum component of the free energies of solvation for NBrCl<sub>2</sub> and NBr<sub>3</sub> was computed with the aug-cc-pVTZ basis set due to computational costs. <sup>f</sup>The standard free energy of formation of H<sub>2</sub>O in water is given at the 55.56 M pure liquid standard state instead of the 1 M aqueous standard state.

model and the M05<sup>114</sup>/aug-cc-pVTZ model chemistry. The SMD solvent method has been found to perform well in the calculations of free energies of solvation for pK<sub>a</sub> predictions.<sup>103,104</sup> Further details are provided in the SI. The resulting computed pK<sub>a</sub><sup>uncorrected</sup> values were substituted into the regression functions established by two linear free energy relationships, as explained below.

To construct a theoretical LFER for cationic ammonium functional groups, we fitted a linear regression between theoretical pK<sub>a</sub><sup>uncorrected</sup> values and previously reported experimental pK<sub>a</sub> values for ammonium,<sup>115</sup> monochlorammonium,<sup>4</sup> chloromethylammonium,<sup>4</sup> methylammonium,<sup>115</sup> dimethylammonium,<sup>116</sup> bromodimethylammonium,<sup>70</sup> trimethylammonium,<sup>117</sup> anilinium,<sup>118</sup> 2-chloranilinium,<sup>118</sup> 2-bromoanilinium,<sup>118</sup> N-methylanilinium,<sup>118</sup> hydroxylammonium,<sup>119</sup> protonated hydrazine,<sup>120</sup> carbamidium (protonated urea),<sup>121</sup> acetamidium (protonated acetamide),<sup>121</sup> and thiocarbamidium (protonated thiourea).<sup>121</sup> This LFER was used to estimate the computed pK<sub>a</sub> values of the cationic species monobromammonium, dibromammonium, dichlorammonium, bromomethylammonium, chloromethylammonium, dibromomethylammonium, and dichloromethylammonium.

To construct a theoretical LFER describing the acidity constant of the neutral amine functional group, we conducted a linear regression between theoretical pK<sub>a</sub><sup>uncorrected</sup> values and previously reported experimental pK<sub>a</sub> data of hydrazoic acid,<sup>122</sup> acetamide,<sup>122</sup> sulfamide,<sup>123</sup> and trifluoromethanesulfamide.<sup>122</sup> The resulting LFER was employed to estimate the computed pK<sub>a</sub> values of monochloramine, monobromamine, dichloramine, dibromamine, and bromochloramine.

## RESULTS AND DISCUSSION

**Evaluation of Solvent Models for Halogen Species and Amines.** We evaluated six different solvent modeling approaches for their abilities to predict the free energies of solvation for species that are structurally related to the halamines. Four implicit solvent models (SMD, CPCM, PCM, and COSMO) and two cluster-continuum approaches

were applied to Cl<sub>2</sub>, Br<sub>2</sub>, NF<sub>3</sub>, NH<sub>3</sub>, H<sub>2</sub>O, NH<sub>2</sub>CH<sub>3</sub> and NH(CH<sub>3</sub>)<sub>2</sub> which we denoted as test set A (Table 1). Experimental Henry's law constants are available for these seven species (SI Table S1),<sup>124–126</sup> with corresponding experimental free energy of solvation ( $\Delta G_{\text{solv,Expt}}^*$ ) values that are considered to have uncertainties ranging from ±0.7 kJ mol<sup>-1</sup> to ±2.5 kJ mol<sup>-1</sup> (Table 1). We also tested the solvent models against experimental  $\Delta G_{\text{solv,Expt}}^*$  values of the three chloramines and of hypochlorous acid, which have been assigned larger uncertainties of ±4.2 kJ mol<sup>-1</sup>.<sup>124</sup>

The SMD model and cluster-continuum-SMD approaches exhibit root-mean-square errors (RMSE) of 3.3 kJ mol<sup>-1</sup> and 3.8 kJ mol<sup>-1</sup>, respectively, with respect to  $\Delta G_{\text{solv,Expt}}^*$  values for set A (Table 1). For compound set B, which contains compounds having more uncertain experimental values, the two models produced larger RMSE values of 5.5 kJ mol<sup>-1</sup> and 4.9 kJ mol<sup>-1</sup>, respectively. The average unsigned error observed for SMD with test set A (3.1 kJ mol<sup>-1</sup>) is very similar to the average unsigned errors that ranged from 2.5 to 3.8 kJ mol<sup>-1</sup> (depending on the DFT method) reported elsewhere<sup>86</sup> for SMD with a very large test set of small neutral molecules in water. The COSMO, CPCM, and PCM models produced worse results for this chemical test set (SI Table S3), and these models were thus viewed as less appropriate for investigating the solvation of halamines in water.

Based on the above results, it is difficult to distinguish whether the SMD implicit model or the cluster-continuum-SMD approach would perform the best for estimating the free energies of solvation of bromamines, chloramines, and bromochloramines. Closer inspection of Table 1 results is revealing. Compared to the conventional SMD implicit model, the addition of an explicit water (i.e., cluster-continuum-SMD approach) improves, but “overcorrects”, the predictions of Henry's law constants for the polar molecules NH<sub>3</sub> and H<sub>2</sub>O. In contrast, the cluster-continuum-SMD approach appears to worsen slightly the results for the halogen-containing species (Cl<sub>2</sub>, Br<sub>2</sub>, NF<sub>3</sub>), compared to conventional SMD. Taken together, these results suggest that a “half-and-half” approach,

**Table 3. Equilibrium Constants (LogK<sub>aq</sub>) for Reactions Leading to Halamines in Water: Computational and Experimental Estimates**

#	reactions	logK <sub>aq</sub> <sup>Comp<sup>a</sup></sup>	logK <sub>aq</sub> <sup>Eq.9<sup>b</sup></sup>	logK <sub>aq</sub> <sup>Expt</sup>
chloramines				
1	$\text{NH}_{3,\text{aq}} + \text{HOCl}_{\text{aq}} \xrightleftharpoons{K_1} \text{NH}_2\text{Cl}_{\text{aq}} + \text{H}_2\text{O}_1$	11.4 ± 1.1	10.6 ± 0.8	11.3 <sup>c</sup> , 8.2 <sup>d</sup>
2	$\text{NH}_2\text{Cl}_{\text{aq}} + \text{HOCl}_{\text{aq}} \xrightleftharpoons{K_2} \text{NHCl}_{2,\text{aq}} + \text{H}_2\text{O}_1$	10.9 ± 1.1	10.7 ± 0.8	8.7 <sup>e</sup>
3	$\text{NHCl}_{2,\text{aq}} + \text{HOCl}_{\text{aq}} \xrightleftharpoons{K_3} \text{NCl}_{3,\text{aq}} + \text{H}_2\text{O}_1$	10.7 ± 1.1	8.7 ± 0.8	4.7 <sup>e</sup> , 8.2 <sup>e</sup> , 7.5 <sup>d</sup>
bromamines				
4	$\text{NH}_{3,\text{aq}} + \text{HOBr}_{\text{aq}} \xrightleftharpoons{K_4} \text{NH}_2\text{Br}_{\text{aq}} + \text{H}_2\text{O}_1$	9.3 ± 1.1		10.5 <sup>f</sup>
5	$\text{NH}_2\text{Br}_{\text{aq}} + \text{HOBr}_{\text{aq}} \xrightleftharpoons{K_5} \text{NHB}_{2,\text{aq}} + \text{H}_2\text{O}_1$	8.8 ± 1.2		8.7 <sup>f</sup>
6	$\text{NHB}_{2,\text{aq}} + \text{HOBr}_{\text{aq}} \xrightleftharpoons{K_6} \text{NBr}_{3,\text{aq}} + \text{H}_2\text{O}_1$	10.1 <sup>g</sup> ± 1.2		6.7 <sup>f</sup>
bromochloramines				
7	$\text{NH}_2\text{Br}_{\text{aq}} + \text{HOCl}_{\text{aq}} \xrightleftharpoons{K_7} \text{NHB}_{\text{r}}\text{Cl}_{\text{aq}} + \text{H}_2\text{O}_1$	11.8 ± 1.2		
8	$\text{NH}_2\text{Cl}_{\text{aq}} + \text{HOBr}_{\text{aq}} \xrightleftharpoons{K_8} \text{NHB}_{\text{r}}\text{Cl}_{\text{aq}} + \text{H}_2\text{O}_1$	9.8 ± 1.2		
9	$\text{NHB}_{\text{r}}\text{Cl}_{\text{aq}} + \text{HOCl}_{\text{aq}} \xrightleftharpoons{K_9} \text{NBr}_{\text{r}}\text{Cl}_{2,\text{aq}} + \text{H}_2\text{O}_1$	9.2 <sup>g</sup> ± 1.2		
10	$\text{NHB}_{\text{r}}\text{Cl}_{\text{aq}} + \text{HOBr}_{\text{aq}} \xrightleftharpoons{K_{10}} \text{NBr}_{\text{r}}\text{Cl}_{2,\text{aq}} + \text{H}_2\text{O}_1$	8.7 ± 1.2		
11	$\text{NHCl}_{2,\text{aq}} + \text{HOBr}_{\text{aq}} \xrightleftharpoons{K_{11}} \text{NBr}_{\text{r}}\text{Cl}_{2,\text{aq}} + \text{H}_2\text{O}_1$	8.1 <sup>g</sup> ± 1.2		
12	$\text{NHB}_{\text{r}}\text{Cl}_{2,\text{aq}} + \text{HOCl}_{\text{aq}} \xrightleftharpoons{K_{12}} \text{NBr}_{\text{r}}\text{Cl}_{2,\text{aq}} + \text{H}_2\text{O}_1$	11.7 ± 1.2		
disproportionation reactions				
13	$\text{NH}_2\text{Cl}_{\text{aq}} + \text{NH}_2\text{Cl}_{\text{aq}} \xrightleftharpoons{K_{13}} \text{NHCl}_{2,\text{aq}} + \text{NH}_{3,\text{aq}}^{\text{h}}$	-0.5 ± 1.1	0.1 ± 0.8	-2.6 <sup>i</sup>
14	$\text{NH}_2\text{Br}_{\text{aq}} + \text{NH}_2\text{Br}_{\text{aq}} \xrightleftharpoons{K_{14}} \text{NHB}_{2,\text{aq}} + \text{NH}_{3,\text{aq}}^{\text{j}}$	-0.5 ± 1.2		0.5 <sup>k</sup>
15	$\text{NH}_2\text{Cl}_{\text{aq}} + \text{NH}_2\text{Br}_{\text{aq}} \xrightleftharpoons{K_{15}} \text{NHB}_{\text{r}}\text{Cl}_{\text{aq}} + \text{NH}_{3,\text{aq}}$	0.4 ± 1.2		
16	$\text{NHB}_{\text{r}}\text{Cl}_{\text{aq}} + \text{HOCl}_{\text{aq}} \xrightleftharpoons{K_{16}} \text{NHCl}_{2,\text{aq}} + \text{HOBr}_{\text{aq}}$	1.1 ± 1.2		
17	$\text{NHB}_{\text{r}}\text{Cl}_{\text{aq}} + \text{HOBr}_{\text{aq}} \xrightleftharpoons{K_{17}} \text{NHB}_{2,\text{aq}} + \text{HOCl}_{\text{aq}}$	-3.0 ± 1.2		
18	$2\text{NH}_2\text{Cl}_{\text{aq}} + \text{Br}_{\text{aq}}^- + \text{H}_{\text{aq}}^+ \xrightleftharpoons{K_{18}} \text{NHB}_{\text{r}}\text{Cl}_{\text{aq}} + \text{NH}_{4,\text{aq}}^+ + \text{Cl}_{\text{aq}}^-$	12.0 <sup>l</sup>		

<sup>a</sup>These estimates were calculated using eqs 6 and 7. Uncertainty bounds are assigned such that the prediction is expected to contain the correct experimental value in 95% of cases. <sup>b</sup>These estimates were calculated using eq 9. <sup>c</sup>This logK<sub>aq</sub><sup>Expt</sup> value was obtained from Morris and Isaac's fitting model.<sup>5</sup> <sup>d</sup>These values were taken from Soulard et al.<sup>12</sup> <sup>e</sup>This experimental value was taken from Kumar and co-workers.<sup>66</sup> <sup>f</sup>These values were taken from Hofmann and Andrews' review.<sup>68</sup> <sup>g</sup>Exceptionally, the free energies of solvation for the reactions leading to NBrCl<sub>2</sub> and NBr<sub>3</sub> were computed with the aug-cc-pVTZ basis set, due to the computational cost of computations with larger basis sets. <sup>h</sup>This reaction can take place by two parallel pathways: a neutral uncatalyzed pathway and also an acid-catalyzed pathway. The computed and experimental equilibrium constant values reported here refer to the uncatalyzed reaction.<sup>128</sup> <sup>i</sup>These values were taken from Morris and Isaac's work.<sup>5</sup> <sup>j</sup>This reaction can take place by two parallel pathways: a neutral uncatalyzed pathway and also an acid-catalyzed pathway. The computed and experimental equilibrium constant values reported here refer to the uncatalyzed reaction.<sup>5</sup> <sup>k</sup>This value was taken from Lei et al.<sup>8</sup> <sup>l</sup>This value was derived using the theoretical aqueous standard free energy of formation for NH<sub>2</sub>Cl and NHB<sub>r</sub>Cl (Table 2) and the previously reported experimental standard free energy of formation<sup>127</sup> for H<sub>aq</sub><sup>+</sup>, Br<sub>aq</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and Cl<sub>aq</sub><sup>-</sup>.

formulated as an average of the predictions by both solvent models, would produce the most accurate results overall for the related molecules, chloramines and bromamines. The "half-and-half" approach exhibits a RMSE of 3.2 kJ mol<sup>-1</sup> in the free energies of solvation of set A. Based on these considerations, we propose that the error bounds expected to contain 95% of the deviations can be approximated by 2 × RMSE found for the free energy of solvation data, and thus we assign an error of 6 kJ mol<sup>-1</sup> to the free energy of solvation values estimated from the "half-and-half" approach for chloramines, bromamines, and bromochloramines (Table 2).

**Estimated Aqueous Standard Free Energies of Formation for Chloramines, Bromamines, and Bromochloramines.** We estimated aqueous standard free energies of formation of halamines and related compounds (Table 2) based on theoretically determined standard free energies of formation in gas phase, Δ<sub>f</sub>G<sub>gas,Comp</sub><sup>o</sup>(X), and computationally estimated free energies of solvation, ΔG<sub>solv,half-and-half</sub><sup>\*</sup>(X), according to

$$\Delta_f G_{\text{aq,Comp}}^*(X) = \Delta_f G_{\text{gas,Comp}}^o(X) + \Delta G_{\text{solv,half-and-half}}^*(X) + \Delta G^{\text{o} \rightarrow *}$$
(6)

Theoretical benchmark  $\Delta_f G_{\text{gas,Comp}}^{\circ}(X)$  values at 1 atm standard state were taken from recently published data.<sup>76,77</sup> The  $\Delta G_{\text{solv,half-and-half}}^*(X)$  values were obtained from an average of the SMD implicit solvent model results and the cluster-continuum-SMD results as discussed in the previous section. The term  $\Delta G^{\circ \rightarrow *}$  represents the free energy required to transfer a molecule from the gas phase 1 atm standard state to the aqueous 1 M standard state.<sup>78</sup>

For computational  $\Delta_f G_{\text{aq,Comp}}^*$  data, we assigned uncertainty bounds such that the computational predictions are expected to contain the correct experimental value in 95% of cases, as follows. In a previous study, we attributed an uncertainty of 1 kJ mol<sup>-1</sup> to the  $\Delta_f G_{\text{gas,Comp}}^{\circ}$  of the three chloramines and of monobromamine, whereas we assigned an uncertainty of 3 kJ mol<sup>-1</sup> to the  $\Delta_f G_{\text{gas,Comp}}^{\circ}$  values of bromochloramines, dibromamine, and tribromamine, based on comparisons between theoretical and experimental data discussed in that paper and citations therein.<sup>76,77</sup> Based on the results discussed in the previous section (Table 1), the  $\Delta G_{\text{solv,half-and-half}}^*$  values predicted with the “half-and-half” approach (an average of the SMD and the cluster-continuum-SMD values) are assigned an uncertainty of 6 kJ mol<sup>-1</sup>. Based on propagation of error (SI eqs S11 and S12), we estimated an error of 6 kJ mol<sup>-1</sup> for the  $\Delta_f G_{\text{aq,Comp}}^*$  values of chloramines, NH<sub>3</sub>, H<sub>2</sub>O, HOCl, HOBr, and NH<sub>2</sub>Br, and an error of 7 kJ mol<sup>-1</sup> for the  $\Delta_f G_{\text{aq,Comp}}^*$  values of dibromamine, tribromamine, and the three bromochloramines. For the well-characterized molecules NH<sub>3</sub> and H<sub>2</sub>O, the theoretical  $\Delta_f G_{\text{aq,Comp}}^*$  values differ from the experimental  $\Delta_f G_{\text{aq,Expt}}^*$  values by only 2.3 and 1.1 kJ mol<sup>-1</sup>, respectively (Table 2). However, for the chloramines and bromamines, there is less consistent agreement between theoretical and experimental results, and some of the previously reported experimental data show large discrepancies from one another. A critical discussion of these different data sets is explored in the following section on aqueous equilibrium constants.

**Aqueous Equilibrium Constants of Reactions that Produce Chloramines, Bromamines, and Bromochloramines.** Despite the wide importance of halamines in drinking water treatment, equilibrium constants have not been well-constrained for many of the reactions responsible for their occurrence. We determined equilibrium constants ( $K_{\text{aq}}^{\text{Comp}}$ ) for several important reactions, based on theoretical  $\Delta_f G_{\text{aq,Comp}}^*$  data (Table 2), and we compared these  $K_{\text{aq}}^{\text{Comp}}$  values to previously reported experimental estimates, where available.

For a reaction in aqueous solution, we can evaluate the aqueous free energy of reaction,  $\Delta G_{\text{aq}}^*$ :

$$\Delta G_{\text{aq}}^* = \sum_i \nu_i \Delta_f G_{\text{aq}}^*(X_i) \quad (7)$$

where the  $\nu_i$  is the stoichiometric coefficient of molecule  $X_i$  and  $\Delta_f G_{\text{aq}}^*(X_i)$  is the aqueous standard Gibbs free energy of formation for species  $X_i$  at 1 M standard state. For those reactions that generate water as a product, we applied a standard state conversion so that H<sub>2</sub>O is at the liquid water (55.56 M) standard state (Table 2).<sup>78</sup> Further details on standard state conversion factors are provided in the SI. The computed aqueous equilibrium constant for a given reaction is obtained by

$$K_{\text{aq}} = \exp\left(\frac{-\Delta G_{\text{aq}}^*}{RT}\right) \quad (8)$$

Theoretical equilibrium constant data,  $K_{\text{aq}}^{\text{Comp}}$ , reveal that reactions of ammonia with HOCl and HOBr that produce mono-, di-, and trihalogenated species are highly favorable, with  $\log K_{\text{aq}}^{\text{Comp}}$  values ranging from 8.1 to 11.8 (reactions 1–12, Table 3). The considered disproportionation reactions that involved neutral species (reactions 13–17, Table 3) were found to have  $\log K_{\text{aq}}^{\text{Comp}}$  values ranging from –3.0 to 1.1. Based on the uncertainties ascribed to  $\Delta_f G_{\text{aq,Comp}}^*$  values (Table 2), we assigned an error of  $\pm 1.1$  to  $\pm 1.2$  logarithmic unit to  $\log K_{\text{aq}}^{\text{Comp}}$  values, depending on the reaction.

In previous reports, equilibrium constants have been estimated based on experimental data for several reactions that produce halamines. Morris and Isaac reported an aqueous equilibrium constant value,  $K_{\text{aq}}^{\text{Expt}}$ , of  $10^{11.3}$  for the reaction leading to NH<sub>2</sub>Cl (reaction 1, Table 3), a value of  $10^{8.7}$  for the reaction leading to NHCl<sub>2</sub> (reaction 2), and a value of  $10^{4.7}$  for the reaction leading to NCl<sub>3</sub> (reaction 3).<sup>5</sup> However, Kumar and co-workers<sup>66</sup> proposed an estimate of  $10^{8.2}$  for  $K_3$ , 4 orders of magnitude higher than the value suggested by Morris and Isaac. The equilibrium constants reported by Morris and Isaac<sup>5</sup> and by Kumar et al.<sup>66</sup> were deduced based on the measurements of forward and reverse rate constants for these reactions. This discrepancy between different studies reflects the difficulties encountered during the measurements of rate constants used to deduce the equilibrium constants of these reactive species in water. Hofmann and Andrews estimated aqueous equilibrium constants for the production of bromamines,<sup>68</sup> based on estimated standard free energies of formation of bromamines taken from Sugam and Helz's work.<sup>69</sup> The aqueous equilibrium constant of one disproportionation reaction was estimated: the disproportionation of two molecules of monochloramine to form dichloramine (reaction 13).<sup>5</sup> The origins of some of these equilibrium constant data are discussed further in the section about rate constants, below.

We compared our theoretical aqueous equilibrium constant values,  $K_{\text{aq}}^{\text{Comp}}$ , with available estimates obtained from reported experimental data,  $K_{\text{aq}}^{\text{Expt}}$ . We found good agreement between our theoretical aqueous equilibrium constants and previously reported experimental values for the reactions leading to monochloramine (reaction 1), monobromamine (reaction 4), and dibromamine (reaction 5): the experimental and computational equilibrium constants for these reactions agree within 1 order of magnitude, which falls within the error bounds of the theoretical values (Table 3). We viewed that the experimental equilibrium constants reported for reactions 1 and 4 were reliable values, since both the forward and reverse rate constants can be measured under well-controlled conditions for these two reactions. We consider these findings as a validation of the theoretical approach, further confirming the validations of  $\Delta_f G_{\text{gas,Comp}}^{\circ}$ ,  $\Delta G_{\text{solv,half-and-half}}^*$  and  $\Delta_f G_{\text{aq,Comp}}^*$  data, discussed above. However, the agreement between experimental and theoretical results decreases substantially for the reactions that produce dichloramine (reaction 2, Table 3), trichloramine (reaction 3), and tribromamine (reaction 6), as well as the disproportionation reaction 13. Theoretical  $K_{\text{aq}}^{\text{Comp}}$  values for these reactions are  $\sim 2$  to 5 orders of magnitude higher than the experimental equilibrium constants. The discrepancies observed for reactions 2, 3, 6, and 13 might be attributed to the difficulty in performing well-controlled experiments on these species.<sup>5</sup> The experimental equilibrium constant values for reactions 2, 3, 6, and 13 are not direct measurements; rather, they are constrained from kinetic and thermodynamic models that involve multiple reactions.<sup>5,69</sup>

**Table 4.** New Estimates of Reverse Rate Constant Values for Selected Reactions that Produce Chloramines, Bromamines, and Bromochloramines

# <sup>a</sup>	reaction	$k_{f,rxn}^{Expt}$	$k_{r,rxn}^{eq,10b}$	$k_{r,rxn}^{Expt}$
1	$NH_{3,aq} + HOCl_{aq} \xrightleftharpoons[k_{-1}]{k_1} NH_2Cl_{aq} + H_2O_l$	$4.2 \times 10^6 M^{-1} s^{-1c}$	$2 \times 10^{-5} s^{-1}$	$2.1 \times 10^{-5} s^{-1c}$
2	$NH_2Cl_{aq} + HOCl_{aq} \xrightleftharpoons[k_{-2}]{k_2} NHCl_{2,aq} + H_2O_l$	$3.5 \times 10^2 M^{-1} s^{-1c}$	$5 \times 10^{-9} s^{-1}$	$7.6 \times 10^{-7} s^{-1c}$
4	$NH_{3,aq} + HOBr_{aq} \xrightleftharpoons[k_{-4}]{k_4} NH_2Br_{aq} + H_2O_l$	$7.50 \pm 0.4 \times 10^7 M^{-1} s^{-1d}$	$4 \times 10^{-2} s^{-1}$	
8	$NH_2Cl_{aq} + HOBr_{aq} \xrightleftharpoons[k_{-8}]{k_8} NHBrCl_{aq} + H_2O_l$	$2.86 \pm 0.06 \times 10^5 M^{-1} s^{-1e}$	$5 \times 10^{-5} s^{-1}$	
13	$NH_2Cl_{aq} + NH_2Cl_{aq} \xrightleftharpoons[k_{-13}]{k_{13}} NHCl_{2,aq} + NH_{3,aq}^f$	$5.6 \times 10^{-2} M^{-1} s^{-1c}$	$0.2 M^{-1} s^{-1}$	$24 M^{-1} s^{-1c}$

<sup>a</sup>Reaction number is taken from Table 3. <sup>b</sup>Estimates were calculated using eq 10. <sup>c</sup>Experimental values were taken from Morris and Isaac's work.<sup>5</sup> <sup>d</sup>Experimental value was taken from Wajon and Morris.<sup>11</sup> <sup>e</sup>Experimental value was taken from Gazda and Margerum.<sup>51</sup> <sup>f</sup>This reaction can take place by two parallel pathways: a neutral uncatalyzed pathway and also an acid-catalyzed pathway. The calculated and experimental rate constant values reported here refer to the uncatalyzed reaction.<sup>128</sup>

Based on the expected uncertainty of our theoretical data, we infer that the theoretical equilibrium constant values have higher confidence than the previously reported experimental estimates for the reactions 2, 3, 6, and 13. These findings imply that the reactions that produce dichloramine, trichloramine, and tribromamine are more thermodynamically favorable than was previously estimated. Therefore, under circumneutral conditions conducive to the production of chloramines and/or bromamines, the equilibrium concentrations of the dichloramine, trichloramine, and tribromamine species are higher than what previous models have suggested.

For further validation of our theoretical equilibrium constant values,  $K_{aq}^{Comp}$ , we compare them to a second set of estimates, referred to as  $K_{aq}^{eq,9}$ . These values were determined based on the theoretical  $\Delta_f G_{gas,Comp}^o$  values (Table 2) combined with previously reported experimental Henry's law constants, where available:

$$K_{aq}^{eq,9} = \exp\left(\frac{-\sum_i \nu_i (\Delta_f G_{gas,Comp}^o(X_i) + \Delta C_{sol,Expt}^*(X_i) + \Delta G^{o \rightarrow *})}{RT}\right) \quad (9)$$

Based on available experimental reports of Henry's law constants, we determined the  $K_{aq}^{eq,9}$  for reactions involving chloramines (reactions 1, 2, 3, and 13, Table 3). We assigned an uncertainty of 0.8 log unit to the  $\log K_{aq}^{eq,9}$  values based on the uncertainty of 1 kJ mol<sup>-1</sup> attributed to  $\Delta_f G_{gas,Comp}^o$  and the uncertainty of 4.2 kJ mol<sup>-1</sup> associated with the  $\Delta C_{sol,Expt}^*$ .

The resulting  $K_{aq}^{eq,9}$  values for reactions 1, 2, and 13 (Table 3) all exhibit good agreement with  $K_{aq}^{Comp}$  estimates obtained from the theoretical  $\Delta G_{aq}^*$  given by eq 6, which offers mutual validation of these two data sets. Exceptionally, the  $K_{aq}^{eq,9}$  value for reaction 3 disagrees with  $K_{aq}^{Comp}$  by a factor of 100. This discrepancy for reaction 3 is attributed to additive disagreement between  $\Delta G_{sol,Expt}^*$  and  $\Delta G_{sol,half-and-half}^*$  values for the compounds HOCl and NHCl<sub>2</sub> (Table 1), which propagates into the free energies used to determine  $K_{aq}^{eq,9}$  (eq 9) and  $K_{aq}^{Comp}$  (eq 6), respectively. In contrast, the  $K_{aq}^{eq,9}$  values for reactions 2, 3, and 13 are up to 4 orders of magnitude higher than the reported experimental estimates. These data further confirm the above conclusion that the theoretical estimates of the present

study improve upon some of the previously reported experimental estimates for reactions 2, 3, 6, and 13.

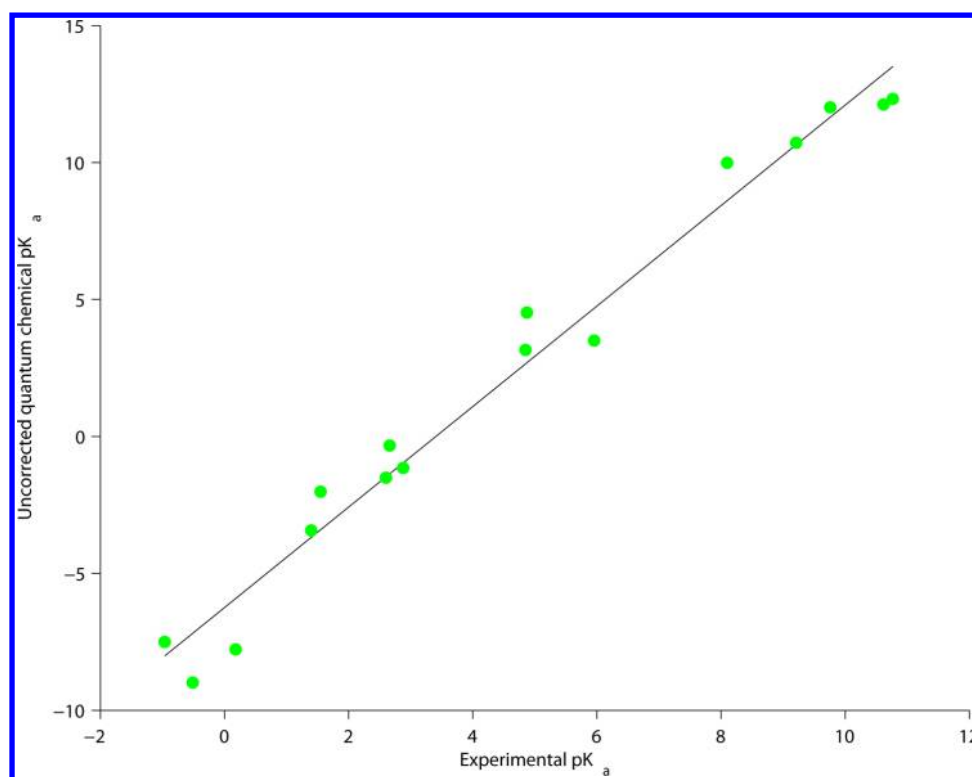
We also estimated the aqueous equilibrium constant for the disproportionation reaction between two molecules of NH<sub>2</sub>Cl and Br<sup>-</sup> (reaction 18, Table 3). We combined theoretical aqueous standard free energies of formation for the NH<sub>2</sub>Cl and NHBrCl species from Table 2 together with reported experimental aqueous standard free energies of formation<sup>127</sup> for the remaining compounds, H<sup>+</sup>, Br<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and Cl<sup>-</sup>. Since we could not find uncertainty bounds for the experimental aqueous standard free energy of formation data, we did not assign an uncertainty value to this equilibrium constant.

## ■ IMPLICATIONS FOR REACTION RATE CONSTANTS

Based on the theoretical aqueous equilibrium constants presented here (Table 3), we can re-evaluate rate constant data for some of the decomposition reactions for chloramines, bromamines, and bromochloramines. For this purpose, we took advantage of the relationship between the reaction equilibrium constant, the forward reaction rate constant, and the reverse reaction rate constant:<sup>129</sup>

$$k_r^{eq,10} = \frac{k_f^{Expt}}{K_{aq}^{Comp}} \quad (10)$$

We assumed that the forward experimental rate constant ( $k_f^{Expt}$ ) had been determined reliably by experiment in previous reports for the five reactions shown in Table 4. Equilibrium constant values ( $K_{aq}^{Comp}$ ) were taken from our theoretical results (Table 3). We compared our theoretically supported estimates of the reverse rate constant for the production of monochloramine,  $k_{-1}^{eq,10}$ , to the previously reported experimental value,  $k_{-1}^{Expt}$ . By way of eq 10, our theoretical estimate,  $k_{-1}^{eq,10} = 2 \times 10^{-5} s^{-1}$ , is in good agreement with the experimental value,  $k_{-1}^{Expt} = 2.1 \times 10^{-5} s^{-1}$ .<sup>5</sup> The agreement between  $k_{-1}^{Expt}$  and  $k_{-1}^{eq,10}$  is consistent with the observed agreement between  $K_1^{Comp}$  and  $K_1^{Expt}$  for this reaction (Table 3). For the chlorination reaction of monochloramine to form dichloramine, we determined a theoretical reverse rate constant of  $k_{-2}^{eq,10} = 5 \times 10^{-9} s^{-1}$ , based on the reported experimental value of the forward reaction (Table 4)



**Figure 1.** Correlation between the experimental  $pK_a$  values and the uncorrected quantum chemical  $pK_a^{\text{uncorrected}}$  results for the ammonium functional group of several compounds, including some halamines for which data are available (SI Table S5).

and the theoretical equilibrium constant,  $K_{\text{aq}}^{\text{Comp}} = 10^{10.9 \pm 1.1}$  (Table 3). The resulting value of  $5 \times 10^{-9} \text{ s}^{-1}$  for the rate constant of the hydrolysis of dichloramine,  $k_{-2}^{\text{eq},10}$ , disagrees with the experimental value ( $7.6 \times 10^{-7} \text{ s}^{-1}$ ) by a factor of 152. The origin of this discrepancy is explained as follows. Morris and Isaac determined the equilibrium constant for reaction 2 as a ratio of the experimental equilibrium constant ( $K_{13}^{\text{Expt}}$ ) of the formation of monochloramine ( $10^{11.3}$ , Table 4) and the experimental equilibrium constant,  $K_{13}^{\text{Expt}} = 10^{-2.6}$  of the disproportionation of  $\text{NH}_2\text{Cl}$  to  $\text{NHCl}_2$  (reaction 13). These authors then used their estimate of the equilibrium constant of reaction 2 together with their experimental forward rate constant (Table 4) to deduce an experimental reverse rate constant for reaction 2. However, the value of  $K_{13}^{\text{Expt}}$  of reaction 13 deviates from our theoretical equilibrium constant ( $K_{13}^{\text{Comp}} = 10^{-0.5 \pm 1.1}$ ). The discrepancy observed for the experimental equilibrium constant for the disproportionation reaction of monochloramine (reaction 13) propagates to the aqueous equilibrium constant for the chlorination reaction of monochloramine (reaction 2). Based on these considerations, we propose our value of the reverse rate constant,  $k_{-2}^{\text{eq},10} = 5 \times 10^{-9} \text{ s}^{-1}$ , as a better alternative to the previous estimate,  $7.6 \times 10^{-7} \text{ s}^{-1}$ .

For the disproportionation reaction of two molecules of monochloramine to form dichloramine (reaction 13), we estimated a theoretical reverse rate constant,  $k_{-13}^{\text{eq},10}$ , of  $0.2 \text{ M}^{-1} \text{ s}^{-1}$ , based on the rate constant for the forward reaction reported by Morris and Isaac,  $k_{13}^{\text{Expt}} = 5.6 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ , and the theoretical aqueous equilibrium constant of  $K_{13}^{\text{Comp}} = 10^{-0.5 \pm 1.1}$ . The resulting theoretically supported value of  $k_{-13}^{\text{eq},10}$ ,  $0.2 \text{ M}^{-1} \text{ s}^{-1}$ , is 2 orders of magnitude lower than the experimental estimate ( $k_{-13}^{\text{Expt}} = 24 \text{ M}^{-1} \text{ s}^{-1}$ ). We interpret that this discrepancy arises from the experimental aqueous

equilibrium constant,  $K_{13}^{\text{Expt}} = 10^{-2.6,5}$ , which is 2 orders of magnitude lower than the theoretical value,  $K_{13}^{\text{Comp}} = 10^{-0.5 \pm 1.1}$ . Hence, using similar reasoning as for reaction 2 (above), we propose our theoretically supported value of  $k_{-13}^{\text{eq},10}$  as an alternative to the experimentally derived estimate.

Further taking advantage of eq 10, here we provide theoretical estimates of the reverse rate constants for the bromination reactions of ammonia and monochloramine (reactions 4 and 8), based on the previously determined  $k_f^{\text{Expt}}$  values and our theoretical  $K_{\text{aq}}^{\text{Comp}}$  values (Table 3) for these reactions. For reaction 4, we used the forward rate constant value proposed by Wajon and Morris,<sup>11</sup>  $k_4^{\text{Expt}} = 7.5 \pm 0.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . This value was confirmed later by Inman and Johnson<sup>19</sup> who reported a kinetic constant of  $4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , and by Heeb<sup>101</sup> who proposed a value of  $5.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . Our resulting estimate of  $k_{-4}^{\text{eq},10} = 4 \times 10^{-2} \text{ s}^{-1}$  is reasonably consistent (within an expected uncertainty of an order of magnitude) with the value originally reported by Haag and Lietzke,  $1.5 \times 10^{-3} \text{ s}^{-1}$ .<sup>67</sup> For reaction 8, which describes the production of chlorobromamine from the reaction of  $\text{NH}_2\text{Cl}$  with  $\text{HOBr}$ , we assumed the forward rate constant measured by Gazda and Margerum,  $k_8^{\text{Expt}} = 2.86 \pm 0.06 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>51</sup> This value implies a reverse rate constant of  $k_{-8}^{\text{eq},10} = 5 \times 10^{-5} \text{ s}^{-1}$ . Based on the theoretical aqueous equilibrium constants reported here, we were thus able to (re)assess the rate constants of some decomposition and disproportionation reactions involving chloramines, bromamines, and bromochloramines. Similar exercises could be applied to other available rate constant data involving halamines, based on the thermodynamic property data that we have provided in the present work.

**$pK_a$  Values for Chloramines, Bromamines, and Bromochloramines: Theoretical Estimates.** Dissociation constants of chloramines and bromamines are difficult to



**Table 5. Estimated  $pK_a$  Values for the Cationic Conjugate Acid and Neutral Chloramines, Bromamines, Bromochloramines, and Methylated Halamines, According to Quantum Chemical LFER Results (SI Tables S5 and S6, Figure 1, and SI Figure S1)**

deprotonation reactions	$pK_a$	$pK_a$	$pK_a$
	X = Cl	X = Br	X = Cl and Br
$\text{NH}_3\text{X}^+ \xrightleftharpoons{K_a^{\text{NH}_3\text{X}^+}} \text{NH}_2\text{X} + \text{H}^+$	$1.5 \pm 1^a, 1.44^b$	$0.8 \pm 1^a$	
$\text{NH}_2\text{X}_2^+ \xrightleftharpoons{K_a^{\text{NH}_2\text{X}_2^+}} \text{NHX}_2 + \text{H}^+$	$-6.0 \pm 1^a$	$-7.8 \pm 1^a$	$-7.1 \pm 1^a$
$\text{NH}_2\text{XCH}_3 + \xrightleftharpoons{K_a^{\text{NH}_2\text{XCH}_3^+}} \text{NHXCH}_3 + \text{H}^+$	$2.3 \pm 1^a, 1.55^b$	$1.3 \pm 1^a$	
$\text{NHX}(\text{CH}_3)_2 + \xrightleftharpoons{K_a^{\text{NHX}(\text{CH}_3)_2^+}} \text{NX}(\text{CH}_3)_2 + \text{H}^+$		$2.8 \pm 1^a, 2.88^c$	
$\text{NHX}_2\text{CH}_3 + \xrightleftharpoons{K_a^{\text{NHX}_2\text{CH}_3^+}} \text{NX}_2\text{CH}_3 + \text{H}^+$	$-5.0 \pm 1^a$	$-5.9 \pm 1^a$	$-5.4 \pm 1^a$
$\text{NH}_2\text{X} \xrightleftharpoons{K_a^{\text{NH}_2\text{X}}} \text{NHX}^- + \text{H}^+$	$19.7 \pm 1^d$	$24.7 \pm 1^d$	
$\text{NHX}_2 \xrightleftharpoons{K_a^{\text{NHX}_2}} \text{NX}_2^- + \text{H}^+$	$11.8 \pm 1^d$	$19.6 \pm 1^d$	$12.5 \pm 1^d$

<sup>a</sup>The regression line used for this quantum chemical LFER is SI eq S13. <sup>b</sup>Experimental values were taken from Margerum and Gray. <sup>c</sup>Experimental value was taken from Antelo and co-workers. <sup>d</sup>The regression line used for this quantum chemical LFER is SI eq S13.

measure experimentally due to the high reactivities of these molecules in water. We estimated acid dissociation constant values for both the cationic conjugate acid and neutral amine functional group of chloramines, bromamines, bromochloramines, and selected methyl-substituted halamines.

We established a quantum chemical LFER (Table S5 in SI) based on previously reported experimental  $pK_a$  values of 16 substituted ammonium groups. We found a correlation coefficient of  $R^2 = 0.98$  for the regression line of this computational LFER (Figure 1). The following equation was used to determine the computed  $pK_a$  values of several chlorammonium and bromammonium species (Table 5):

$$pK_a^{\text{Quantum Chemical LFER}} = 1.83 \times pK_a^{\text{uncorrected}} - 6.25 \quad (11)$$

We also constructed a quantum chemical LFER (SI Table S6) based on theoretical and experimental  $pK_a$  data of four neutral amine functional groups. The regression line of the LFER (SI eq S13) established to estimate the  $pK_a$  values for neutral halamines had a correlation coefficient  $R^2$  of 0.93 (SI Figure S1). This relationship was used to predict the  $pK_a$  values for neutral chloramines, bromamines, and bromochloramines (Table 5). Uncertainties of the predicted  $pK_a$  values were assigned as  $\pm 1$  log unit, based on previous work on LFER prediction of  $pK_a$  values<sup>95,102,105,106</sup> and on the observed scatter in the fitted LFER data (SI Tables S5 and S6).

Dissociation constants for chloramines, bromamines, bromochloramines, and methyl-substituted halamines reveal the pH-dependent speciation of these reactive molecules in water. Computed  $pK_a$  data show that chloramines and bromamines are predominantly in neutral form at circumneutral pH. However, selected cationic species and anionic species are still relevant for certain reactions. For example,  $\text{NH}_3\text{Br}^+$  was found to predominate over  $\text{NH}_2\text{Br}$  in reactions with substituted phenols studied by Heeb et al. at neutral pH, despite the low  $pK_a$  of monobromammonium ( $\sim 0.8$ ), due to the much higher electrophilicity of monobromammonium relative to monobromamine.<sup>101</sup> On the other hand, the computed  $pK_a$  values of  $\text{NHCl}_2$  and  $\text{NHClBr}$  ( $\sim 11.8$  and  $\sim 12.5$ , respectively) are down-shifted relative to the less acidic monohalogenated species  $\text{NH}_2\text{Cl}$  and  $\text{NH}_2\text{Br}$ , due to the stabilization of the anion by the presence of an additional electron-withdrawing substituent. The resulting deprotonated anionic species may be

relevant for reactions with electrophiles. For example, recent theoretical work indicated that ozone oxidizes primarily the deprotonated anionic form of bromo-*N,N*-dimethylsulfamide rather than the neutral species ( $pK_a \sim 9.0$ ), due to the higher nucleophilicity of the anionic form.<sup>95</sup>

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b03219.

Computational modeling of free energies of solvation and aqueous free energies of reaction; experimental Henry's law constants and conversion factor; assignment of the error bounds for the computed aqueous standard free energies of formation; aqueous free energy of the proton; evaluation of B2PLYPD method for total atomization energies for selected halogen species; evaluation of implicit solvent models for the prediction of free energies of solvation for halamines and related species; evaluation of the gas phase equilibrium constants and the aqueous equilibrium constant values using the SMD and COSMO implicit solvent models and the cluster-continuum-SMD approach; and experimental and quantum chemical computed  $pK_a$  values for neutral chloramines and bromamines and for the cationic conjugate acid ammonium functional groups of several halamines (PDF)

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### Notes

The authors declare no competing financial interest.

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