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Benchmark thermochemistry of chloramines, bromamines, and bromochloramines: halogen oxidants stabilized by electron correlation†

Daniela Trogolo and J. Samuel Arey*‡

Chloramines, bromamines, and bromochloramines are halogen-containing oxidants that arise from the reaction of hypohalous acids with ammonia in water. Although relevant to both water disinfection chemistry and biochemistry, these molecules are difficult to study in the laboratory, and their thermochemical properties remain poorly established. We developed a benchmark level *ab initio* calculation protocol, termed TA14, adapted from the Weizmann theory and Feller–Peterson–Dixon approaches to determine the molecular structures and thermochemical properties of these compounds. We find that the halamine molecules are bound largely, and in some cases entirely, by electron correlation forces. This presumably explains their high reactivity as electrophilic oxidants. We provide computed heats of formation at 0 K ($\Delta_f H^0_{0\,K}$) and at 298 K ($\Delta_f H^0_{298\,K}$) and Gibbs free energies of formation at 298 K ($\Delta_f G^0_{298\,K}$) for the 9 inorganic chloramines, bromamines, bromochloramines in gas phase. Based on comparisons to previous theoretical and experimental data for a set of 11 small molecules containing N, O, H, Cl, and Br, we propose uncertainties ranging from 1 to 3 kJ mol^{-1} for computed thermodynamic properties of the halamines. Reported thermochemical data enable the determination of equilibrium constants for reactions involving halamines, opening possibilities for more quantitative studies of the chemistry of these poorly understood compounds.

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1 Introduction

Halogen-containing oxidants have long received attention, due to their role in processes affecting human health and environmental hygiene.[1,2] Chlorination and chloramination are the predominant methods of drinking water disinfection in the United States.[3–5] Chlorine is commonly applied either as gaseous Cl_2, which dissolves in water at room temperature, or as a salt of hypochlorite, OCl^-:

$$Cl_2 + H_2O \rightarrow HOCl + HCl \quad (1)$$

$$OCl^- + H^+ \overset{pK_a}{\longleftrightarrow} HOCl \quad (2)$$

Cl_2 and hypochlorite both lead to the formation of hypochlorous acid, HOCl (pK_a = 7.5[6]). In ammonia-containing water, HOCl undergoes substitution reactions with ammonia, following a well-known process that leads to the formation of chloramines:[7–11]

$$NH_3 + HOCl \rightleftharpoons NH_2Cl + H_2O \quad (3)$$

$$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O \quad (4)$$

$$NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O \quad (5)$$

Monochloramine can be directly added to water during drinking water disinfection treatment.[3–5,12] Operationally, these reactions are largely controlled by the ratio of chlorine to ammonia nitrogen, pH, temperature, and the presence of natural acid catalysts as phosphate, sulfate, and carbonate.[11,13]

Bromamines and bromochloramines may arise as well, in bromine-containing waters.[14–22] During disinfection treatment, bromide can become oxidized to hypobromous acid/hypobromite, contributing to the formation of bromamines and bromochloramines in water.[23] The role of bromide in monochloramine decay was considered in the kinetic model provided by Vikesland *et al.*[13] Lei *et al.* reported on the formation kinetics of bromamines,[24] and Luh and Mariñas recently investigated the formation kinetics of bromochloramines, providing more information on their aqueous chemistry.[25]

Chloramines and bromamines are implicated in the formation of potentially toxic disinfection byproducts (DBPs) during

Environmental Chemistry Modeling Laboratory, École Polytechnique Fédérale de Lausanne (EPFL), Station 2, 1015 Lausanne, Switzerland.
E-mail: samuel.arey@epfl.ch; Fax: +41 (0)21 693 8070; Tel: +41 (0)21 693 8031

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‡ EAWAG, Swiss Federal Institute of Aquatic Science and Technology, Dübendorf, Switzerland.

water treatment.[3,4,26–28] Chloramines can undergo substitution and oxidation reactions involving natural organic matter.[29] Snyder and Margerum[30] and then Isaac and Morris[31,32] showed that monochloramine could transfer chlorine to organic nitrogen compounds by general acid catalysis. During water disinfection, monochloramine can play a direct role in the formation of halonitriles, halonitroalkanes and nitrosamines.[33] Monochloramine reactions with dissolved organic matter can also lead to production of haloacetic acids.[34] The reaction between dichloramines and organic nitrogen precursors such as dimethylamine can explain the observed production of *N*-nitrosodimethylamine (NDMA) and other nitrosamines,[35,36] which are probable human carcinogens according to the US Environmental Protection Agency. Fewer data are available concerning the role of bromamines and bromochloramines in reactions that lead to DBP formation. Le Roux *et al.* reported an enhancement of the formation of NDMA from reactions between bromine-containing oxidant species and tertiary amines or dimethylamine, suggesting a direct role of bromamines.[27] Monobromamine and dibromamine were also found to react with cyanide ion (CN^-) leading to the formation of CNBr, a volatile DBP.[28] According to Valentine,[37] the bromine atom of bromochloramine is highly reactive. Despite their considerable roles in disinfection byproduct formation, the speciation of chloramines, bromamines, and bromochloramines is not fully known, and this impedes mechanistic studies of DBP formation, which can involve many potential reaction pathways.

Due to the volatility of chloramines,[38,39] these molecules also have implications in the poor air quality in indoor swimming pools. According to Richardson *et al.*,[40] NH_2Cl, $NHCl_2$, NCl_3 can escape into the atmosphere of swimming pool environments. They contribute to the typical smell and irritant properties of the air of these facilities.[41]

Chloramines and bromamines are also released extracellularly by activated mammalian eosinophils and neutrophils (white blood cells).[42,43] The haem enzymes eosinophil peroxidase and myeloperoxidase catalyse the production of HOBr and HOCl that can react with extracellular matrix, including proteins, proteoglycans, and other nitrogen organic compounds, generating substituted bromamines and chloramines.[43–47] The N-bromination reactions promoted by HOBr, which exhibits higher rate constants than the corresponding reactions by HOCl, may damage tissue, affecting cellular and tissue function, in inflammatory diseases such as asthma.[45] Moreover, the so-generated halamines can undergo one-electron reduction processes that cleave the N–X (where X = Cl or Br) bond.[48,49] Indeed, redox-active metal ions and superoxide radicals can reduce N-halogenated species, leading to the formation of N-centered radicals and radical bromine atoms.[49]

Despite these concerns, halamine speciation is not fully understood and thus the reactivities of halamines with components of natural waters and biological fluids are difficult to study. Halamines are unstable at neutral pH and autodecompose by a complex set of reactions only partially known.[11,13,29] As a consequence, kinetic experiments on chloramine formation cannot be always successfully conducted under realistic water conditions found in water treatment facilities.[11] Additionally, sampling and analysis of the chloramines in the atmosphere is difficult, requiring specific sampling devices and analytical methods.[41] Due to these challenges, fundamental thermochemical properties of halamines have not been extensively determined with experiments either in gas phase or in aqueous phase.

Quantum computational methods could offer more tractable estimates of the thermochemistry of chloramines, bromamines, and bromochloramines. However existing work is limited. In 1997, Milburn *et al.*[50] reported theoretical enthalpy of formation values for inorganic chloramines at MP4[51–54] and QCISD(T)[55] levels of theory. More recently, Rayne and Forest[56] estimated gas phase standard state enthalpies of formation at 298 K ($\Delta_f H^0_{298\,K}$) for 398 species that contained the elements hydrogen through bromine at the G4[57] level, including NH_2Cl, $NHCl_2$, NCl_3, NH_2Br, and $NHBr_2$. This approach produced a MAD (mean absolute deviation) of 2.68 kcal mol^{-1} with respect to experimental $\Delta_f H^0_{298\,K}$ values for 144 compounds. More recently, Rayne and Forest[58] assessed new $\Delta_f H^0_{298\,K}$ values for NH_2Cl, $NHCl_2$, and NCl_3 using G4MP2.[59] These estimates likely have about 2–3 kcal mol^{-1} uncertainties. In 2011, monochloramine was included in the W4-11 dataset:[60] this is the only halamine whose total atomization energy was determined with benchmark accuracy. Finally, thermochemistry estimates remain absent for NBr_3 and for the bromochloramines.

Calculations of energies for compounds containing halogens are not without their difficulties. Therefore chloramines, bromamines, and bromochloramines require a carefully constructed *ab initio* computational recipe, with attention to several fine quantum mechanical effects, in order to obtain accurate thermochemistry data. Since these inorganic molecules contain the heavy elements chlorine and bromine, fine quantum mechanical effects must be evaluated properly if sub-kcal mol^{-1} or sub-kJ mol^{-1} energies are sought. Indeed, the ''gold standard of quantum chemistry'', or CCSD(T) with complete basis-set limit extrapolation, has to be combined with core valence correlation energy calculations and relativistic effects in order to predict accurate thermochemistry for chlorine- and bromine-containing molecules.[61–64] For molecules with elements from the first and second rows, relativistic and core-correlation contributions to bond energies are relatively small,[61,63,65] but these components increase with the size of the atoms involved. For example, Feller *et al.* reported scalar relativistic contributions of -0.14 kcal mol^{-1} and -0.54 kcal mol^{-1} to the total atomization energies (TAE) of Cl_2 and Br_2, respectively.[63] Core-valence correlation components of the TAEs of these molecules were -0.13 kcal mol^{-1} and 0.29 kcal mol^{-1}, respectively.[63] Post-CCSD(T) energy contributions may also be important. The magnitude of post-CCSD(T) effects is small for systems that are reasonably described by a single reference configuration.[61] However, for species affected by severe nondynamical correlation, post-CCSD(T) contributions to the TAE may exceed 1 kcal mol^{-1}.[63,66] Halogen-containing molecules often exhibit severe nondynamical correlation effects; examples include F_2, FO_2, F_2O_2, FO, F_2O, OClO, and ClOO.[65] Hence, for chloramines and bromamines, we suspected that an extension of the correlation treatment beyond CCSD(T) may be needed.

Specialized methods, such as the HEAT (high-accurate extrapolated *ab initio* thermochemistry),[67–69] Weizmann-*n*,[61,70,71]

and Feller–Peterson–Dixon (FPD)[63,64,72] protocols have been designed to estimate accurate thermochemistry even for difficult cases as those described above. W4 provided thermochemical data up to chlorine-containing molecules with a 'benchmark accuracy' of 1 kJ mol^{-1} (0.24 kcal mol^{-1}).[61] The HEAT target accuracy was sub-kJ mol^{-1} for first-row systems, whereas the FPD approach suggested an accuracy of 0.2 to 0.4 kcal mol^{-1} for small molecules up to the third row. The FPD protocol is more flexible, being developed molecule-by-molecule, and has been applied up to bromine-containing species, including BrO, Br_2, HBr, BrF, and BrCl.[63] These computational methods (Weizmann-*n*, FPD) are commonly recognized as benchmarks for small molecules. Although we were inspired by these established methods, we did not apply any of these protocols in their prescribed formulation. The W3 method does not include second order spin–orbit corrections, and W3 treats core–valence correlation energy with only the MTSmall basis set. These choices would not be appropriate for benchmark thermochemistry of molecules containing bromine. On the other hand, the more rigorous W4 and FPD procedures were intractably expensive for the not-so-small halamine species, with available algorithms and hardware. Hence the halamines warranted the development of a tailored computational recipe for the determination of high-accuracy thermochemistry.

In the present study, we calculated high-quality benchmark gas-phase thermochemical data, including total atomization energies, heats of formation at 0 K and at 298 K, and Gibbs free energies of formation at 298 K for chloramines, bromamines, bromochloramines, and other related small halogenated molecules. For this purpose, we developed a computational protocol, termed as TA14 in the remainder of the manuscript, which is adapted from the high-quality Weizmann-*n*, and Feller–Peterson–Dixon (FDP) procedures. TA14 combines a systematic sequence of coupled cluster methods up to CCSDTQ with large correlation consistent basis sets and includes relativistic effects, core–valence electron correlation, and diagonal Born–Oppenheimer correction, aiming for kJ mol^{-1} accuracy with affordable computing time. A test set of small compounds containing chlorine and bromine was chosen to briefly evaluate the performance of the protocol, and comparisons with high-quality experimental values and previously published computational benchmarks are made. This leads to the first published set of high accuracy thermochemistry data for chloramines, bromamines, and bromochloramines.

2 Methods

2.1 Selected molecules of study and reference data

Our chemical set comprised 20 neutral inorganic molecules, divided by chemical composition into non-halamines (set A) and halamines (set B). Set A includes H_2, N_2, O_2, Cl_2, Br_2, HCl, HBr, HOCl, HOBr, H_2O, and NH_3. Set B contains NH_2Cl, $NHCl_2$, NCl_3, NH_2Br, $NHBr_2$, NBr_3, NHBrCl, $NBrCl_2$, and NBr_2Cl.

Experimental enthalpies of formation and experimental total atomization energies were available in the literature for the entire set A. Experimental total atomization energies at 0 K, $TAE_{0\,K}^{Expt}$, heats of formation at 0 K, $\Delta_f H_{0\,K}^{0,Expt}$, and at 298 K, $\Delta_f H_{298\,K}^{0,Expt}$, and Gibbs free energies of formation, $\Delta_f G_{298\,K}^{0,Expt}$, are taken from several sources: CODATA,[73] the Active ThermoChemical Tables,[74,75] JANAF thermochemical database,[76] and NIST Computational Chemistry Comparison and Benchmark DataBase (CCCBDB).[77] In cases where several experimental values were available for the same molecule, the value with the lowest listed uncertainty was selected.

2.2 Model chemistries and basis sets

Hartree–Fock, CCSD,[78] and CCSD(T)[78–80] calculations were carried out using the program CFOUR.[81] CCSDT,[82–84] CCSDT(Q),[85] and CCSDTQ[86–88] calculations were conducted with the MRCC package[89] interfaced to the CFOUR program suite. Scalar relativistic calculations and B2PLYPD[90,91] frequency analysis were conducted using Gaussian09.[92] Second-order molecular spin–orbit components were computed with NWchem.[93]

The basis sets employed in all calculations belong to the correlation consistent family of Dunning and co-workers[94–98] and are abbreviated PVXZ, AVXZ, and AWCVXZ for cc-pVXZ, aug-cc-pVXZ, and aug-cc-pWCVXZ basis set types, respectively, throughout the remainder of the article. The aug-cc-pV(X+d)Z basis sets employed by W*n* methods were not available for bromine. Complete basis-set limit results were achieved using different extrapolation formulae, as explained below.

2.3 Geometries and frequencies

With three exceptions, all reference geometries were obtained at the all-electron (AE)-CCSD(T)/AVQZ level. For $NBrCl_2$, NBr_2Cl, and NBr_3, geometries were optimized at the all-electron (AE)-CCSD(T)/AVTZ level. For open-shell species, single-point energy calculations were based on UHF reference wave functions, whereas the default restricted Hartree–Fock reference was employed for the closed-shell molecules. Due to high spin contamination using an unrestricted reference, O_2 was treated as a restricted open-shell species. The Watts–Gauss–Bartlett[99] (*e.g.*, CFOUR/ACESII) definition of restricted open-shell CCSD(T) was applied. These reference geometries were used for electronic energy calculations, and they are given in the ESI† for all molecules.

Harmonic and anharmonic zero-point vibrational energies were computed at 298 K using analytic second derivatives for the B2PLYPD/AVQZ model chemistry. The VPT2[100,101] approach was applied to compute the anharmonic corrections as implemented in Gaussian09. Anharmonic frequencies are reported in the ESI† for all the halamines and the hypohalous acids. Since Gaussian09 does not allow the calculations of anharmonic frequency contributions for linear molecules, we employed B2PLYPD/AVQZ for harmonic frequency calculations and combined these with experimental anharmonic contributions for diatomic molecules.[102–104] Molecular rotations were determined assuming rigid geometries, thus rotations were assumed uncoupled to vibrations. Based on these frequency data and corresponding B2PLYPD/AVQZ geometries, zero-point vibrational energies and thermal contributions to the gas phase enthalpy and gas phase Gibbs free energy were computed at 298 K in the *NVT* ensemble for all studied molecules.[105]

2.4 Electronic energies

Our methodology for computing the electronic energy was adapted from the recently developed W3, W4, and FPD protocols,[61,63,71] and it is aimed to being an appropriate compromise between computing cost and basis set convergence. By including all terms that can contribute to the energy at the sub-kJ mol^{-1} level, the TA14 protocol allows the determination of high quality electronic energies and thermodynamic properties of halogenated compounds. The protocol applied to compute the electronic energy is purely *ab initio*: no fitted parameters or empirical terms are included.

An overview of the TA14 protocol, together with other highly accurate thermochemistry composite methods, is shown in Table 1. Within the Born–Oppenheimer approximation, the total energy of a compound may be separated into electronic and vibrational contributions. The ground state electronic energy is expressed by the following additivity scheme:

$$\begin{aligned} E_{\mathrm{e}}^{\mathrm{TA14}} &= E_{\mathrm{HF,Extrap}} + \Delta E_{\mathrm{CCSD,Extrap}} \\ &\quad + \Delta E_{\mathrm{(T),Extrap}} + \Delta E_{\mathrm{T-(T),Extrap}} \\ &\quad + \Delta E_{\mathrm{(Q)}} + \Delta E_{\mathrm{Q-(Q)}} + \Delta E_{\mathrm{CORE}} \\ &\quad + \Delta E_{\mathrm{REL}} + \Delta E_{\mathrm{1st\,SO}} + \Delta E_{\mathrm{2nd\,SO}} \\ &\quad + \Delta E_{\mathrm{DBOC}} \end{aligned} \tag{6}$$

In eqn (6), the term $E_{\mathrm{HF,Extrap}}$ is the Hartree–Fock energy, and $\Delta E_{\mathrm{CCSD,Extrap}}$, $\Delta E_{\mathrm{(T),Extrap}}$ and $\Delta E_{\mathrm{T-(T),Extrap}}$ are valence correlation energies, where the label "Extrap" indicates extrapolation to the complete basis-set limit, explained further below. $\Delta E_{\mathrm{CCSD,Extrap}}$ is given by the CCSD energy contribution, and $\Delta E_{\mathrm{(T),Extrap}}$ describes the energy contribution from the perturbative treatment of triple excitations. $\Delta E_{\mathrm{T-(T),Extrap}}$ describes the energy difference between full triples and the perturbative triples approximation. $\Delta E_{\mathrm{(Q)}}$ and $\Delta E_{\mathrm{Q-(Q)}}$ are the perturbative quadruples contribution and the full quadruples contribution, respectively. The resulting frozen core FC-CCSDTQ energy is very close to the frozen-core non-relativistic FullCI limit.[106] ΔE_{CORE} is the last nonrelativistic component of the total energy and describes core–valence correlation effects. The term ΔE_{REL} represents scalar relativistic effects. First-order and second-order spin–orbit corrections are given as $\Delta E_{\mathrm{1st\,SO}}$ and $\Delta E_{\mathrm{2nd\,SO}}$, and ΔE_{DBOC} is the diagonal Born–Oppenheimer correction. Each of these terms is explained in detail below.

To obtain high accuracy estimates of HF and electronic correlation energies, extrapolation techniques can be applied, requiring large correlation-consistent basis sets.[107] We applied the extrapolation formulae proposed in W4 theory for the Hartree–Fock energies and the extrapolation formulae given in W3 theory for the correlation energies to obtain accurate *ab initio* thermochemistry properties. Theoretical results obtained using this approach are labeled "Best" in the remainder of the article. The Hartree–Fock energy extrapolation is based on the Karton–Martin modification[108] of Jensen's formula:[109]

$$E_{\mathrm{HF,"Best"}} = E_X + \frac{E_X - E_{X-1}}{\dfrac{X\exp\left(9\sqrt{X}-\sqrt{X-1}\right)}{X+1} - 1} \tag{7}$$

where the consecutive cardinal numbers $X-1$ and X are the maximum angular momentum quantum number X represented in correlation-consistent basis set (*e.g.*, 3 for AVTZ, 4 for AVQZ, and 5 for AV5Z).[107] $E_{\mathrm{HF,"Best"}}$ represents the $E_{\mathrm{HF,Extrap}}$ term in eqn (6). Eqn (7) was previously found to give an RMS error of 0.00628 kcal mol^{-1} with respect to the Hartree–Fock complete-basis set energy for a set of atoms and diatomic systems with the AV{Q,5}Z basis set pair.[110]

The correlation energy results are extrapolated separately from the Hartree–Fock components. The CCSD energy typically converges more slowly than the Hartree–Fock energy.[111–113]

Table 1 Comparison of the TA14 computational protocol with other benchmark thermochemistry protocols

Component	FPD[63 d]	W3[71]	W4[61]	TA14
Reference geometry	FC-CCSD(T)/AV6Z	FC-CCSD(T)/pV(Q+d)Z	FC-CCSD(T)/pV(Q+d)Z	AE-CCSD(T)/AVQZ
Anharmonic ZPVE	Expt data	CCSD(T)/VTZ+1[a]	CCSD(T)/VTZ+1[a]	B2PLYPD/AVQZ[b]
Electronic energy				
HF extrapolation	AV6Z	AV(Q,5)+dZ	AV(5,6)+dZ	AV(Q,5)Z
Valence CCSD extrapolation	AV6Z	AV(Q,5)+dZ	AV(5,6)+dZ	AV(Q,5)Z
Valence (T) extrapolation	AV6Z	AV(T,Q)+dZ	AV(Q,5)+dZ	AV(T,Q)Z
Valence T–(T) extrapolation	PVQZ	PV(D,T)Z	PV(D,T)Z	PV(T,Q)Z
Valence (Q)		1.25 PVDZ	1.10 PVTZ	PVTZ
Valence Q–(Q)		1.25 PVDZ	1.10 PVDZ	PVDZ
Valence Q	PVTZ			
Valence 5	PVDZ		PVDZ	
Valence 6			PVDZ	
CCSD(T) core shell	PWCV5Z	MTSmall	AWCV(T,Q)Z	AWCV(T,Q)Z
T–(T) core shell			PWCVTZ[c]	
CCSDTQ core shell	PWCVDZ			
Scalar relativistic CCSD(T)	DK-PVTZ	MTSmall	DK-AV(Q+d)Z	DK-AVQZ
First-order atomic spin–orbit correction	Expt data	Expt data	Expt data	Expt data
Second-order molecular spin–orbit correction	CAS-CI/AVTZ-PP			SO-B3LYP/ECP
DBOC	HF/AVTZ		HF/AVTZ	HF/AVQZ, CCSD/AVDZ

[a] See W2,[70] W3[71] and W4[61] protocols. [b] The VPT2 approach was used. [c] W4.2 also includes this higher core shell contribution. [d] This Feller–Peterson–Dixon procedure was defined for Br_2.[63]

The extrapolations to the infinite basis-set limit for several correlation energy contributions were carried out with the two-term $A + B/L^{\alpha}$ expression used extensively in W*n* theories[61,65,70,71] and expressed in this form:

$$E_{\mathrm{CC,\text{``Best''}}} = E_X + \frac{E_X - E_{X-1}}{(X/X-1)^{\alpha} - 1} \qquad (8)$$

Eqn (8) derives from the truncation of the partial-wave expansion of pair correlation energies to just the leading terms, as described by Klopper.[107] The α factor was set equal to 3, as given in the W3 protocol;[71] this contrasts with the W4 approach[61] where $\alpha = 5$ is used for triplet-coupled pair CCSD energies. Hence, the TA14 protocol uses eqn (7) to extrapolate the Hartree–Fock energy ($E_{\mathrm{HF,Extrap}}$ in eqn (6)) and applies eqn (8) for some correlation energies ($\Delta E_{\mathrm{CCSD,Extrap}}$, $\Delta E_{\mathrm{(T),Extrap}}$, $\Delta E_{\mathrm{T-(T),Extrap}}$) and for ΔE_{CORE} in eqn (6) with $\alpha = 3$ throughout.

As recommended by Klopper and co-workers,[111] the (T) valence correlation energy contribution was evaluated separately from the CCSD contributions, with smaller basis sets. The more expensive (T) contribution converges to the basis set limit more quickly than the CCSD correlation energy.[111,112] Our best estimate $\Delta E_{\mathrm{(T),Extrap}}$ energy contributions were calculated with the AV{T,Q}Z basis set pair and were extrapolated using eqn (8).

Post-CCSD(T) contributions to the electronic energy were determined with smaller basis sets. Higher-order correlated energies converge to the complete basis set limit more efficiently than the energies computed at CCSD(T) level.[64,114] In the present work, the $\Delta E_{\mathrm{T-(T),Extrap}}$ term was extrapolated from CCSDT-CCSD(T) energy differences with the PVTZ and PVQZ basis sets. However for $NBrCl_2$, NBr_2Cl, $NHBr_2$, NHBrCl and NBr_3, we instead used the PV{D,T}Z basis set pair, due to computational limitations.

Separately, we also applied the widely used extrapolation method of Halkier for the Hartree–Fock and CCSD, (T), and T–(T) correlation energies, leading to a second estimate of computed thermodynamic properties. Halkier *et al.*[113,115] proposed applying two-term extrapolation procedures based on calculations with hierarchical correlation-consistent basis sets:

$$E_{\mathrm{HF/CC,\text{``Halkier''}}} = \frac{E_X X^3 - E_{X-1}(X-1)^3}{X^3 - (X-1)^3} \qquad (9)$$

Eqn (9) was applied to approximate both Hartree–Fock energies and the above-listed correlation energies at the complete basis-set limit.[113,116] We used the label ''Halkier'' for thermochemical quantities obtained by use of eqn (9) to extrapolate Hartree–Fock and correlation energies.

As explained by Peterson *et al.*,[64] CCSDT(Q) corrections should always be included in order to counterbalance the CCSDT energy contributions, which are typically less close to the FullCI limit than CCSD(T) values. The $\Delta E_{\mathrm{(Q)}}$ contributions were calculated as the CCSDT(Q)-CCSDT energy difference with the PVTZ basis set. For NBr_3 and NBr_2Cl, the $\Delta E_{\mathrm{(Q)}}$ contribution was computed with the PVDZ basis set. $\Delta E_{\mathrm{Q-(Q)}}$ was computed as the energy difference CCSDTQ-CCSDT(Q) with the PVDZ basis set. We chose to apply the UHF reference wave function on the ROHF oxygen molecule in the calculation of quadruple excitation correlation energy contributions. Due to its high computational cost, the CCSDTQ correlation energy was not computed for NBr_3.

For most molecules, ΔE_{CORE} was assessed as the energy difference between all-electron CCSD(T)/AWCV{T,Q}Z and frozen-core CCSD(T)/AWCV{T,Q}Z calculations, applying eqn (8) to extrapolate each energy to the complete basis-set limit. For NHBrCl the ΔE_{CORE} was computed at the AWCVQZ level, whereas for NBr_3 and NBr_2Cl, this contribution was obtained at the AWCVTZ level, due to computational cost, and no extrapolation formula was applied.

Relativistic contributions were computed as follows. Scalar relativistic effects (ΔE_{REL}) are quantitatively recovered within the second-order Douglas–Kroll–Hess approximation,[117–122] and these were obtained from the energy difference between relativistic CCSD(T)/AVQZ-DK and non-relativistic CCSD(T)/AVQZ calculations. Atomic first-order spin–orbit coupling terms, $\Delta E_{\mathrm{1st\,SO}}$, were taken from the experimental fine structure.[123] For heavy elements such as bromine, second-order molecular spin–orbit contributions have non-negligible contributions.[63,124] These energy contributions, $\Delta E_{\mathrm{2nd\,SO}}$, were carried out with SO-DFT calculations at the B3LYP[125,126] level. The CRENBL basis sets and AREPs (averaged relativistic effective potentials) with spin–orbit operators were employed for the non-hydrogen atoms.[127–132] Although implemented with HF/AVTZ in the W4 scheme, post-HF contributions to the diagonal Born–Oppenheimer correction have been better reproduced when including the CCSD energy contribution.[133] ΔE_{DBOC} calculations thus were conducted at CCSD/AVDZ level, where the HF electronic energy contribution was calculated with the AVQZ basis set:

$$\Delta E_{\mathrm{DBOC}} = \Delta E_{\mathrm{DBOC}}^{\mathrm{HF/AVQZ}} + \Delta\Delta E_{\mathrm{DBOC}}^{\mathrm{CCSD/AVDZ}} \qquad (10)$$

2.5 Thermochemical properties

To construct standard enthalpies of formation at 0 K and 298 K at 1 atm pressure, we determined the electronic energies and the total atomization energies of all species. Total atomization energies at the bottom of the theoretical potential energy well ($TAE_e(M)$) and at 0 K ($TAE_{0\,K}(M)$) were calculated *ab initio* as:

$$\mathrm{TAE}_{\mathrm{e}}^{\mathrm{TA14}}(M) = \sum_{i}^{N} E_{\mathrm{e}}^{\mathrm{TA14}}(A_i) - E_{\mathrm{e}}^{\mathrm{TA14}}(M) \qquad (11)$$

$$\mathrm{TAE}_{0\,\mathrm{K}}^{\mathrm{TA14}}(M) = \mathrm{TAE}_{\mathrm{e}}^{\mathrm{TA14}}(M) - \mathrm{ZPVE}^{\mathrm{TA14}}(M) \qquad (12)$$

where $E_{\mathrm{e}}^{\mathrm{TA14}}(M)$ and $E_{\mathrm{e}}^{\mathrm{TA14}}(A_i)$ are the electronic energies of the molecule M and of the constituent atoms A_i, computed following the TA14 protocol, and $\mathrm{ZPVE}^{\mathrm{TA14}}(M)$ is the computed anharmonic zero-point vibrational energy of the molecule.

The method to calculate standard enthalpies of formation has been described previously by Curtiss *et al.*[134] Briefly the procedure was as follows. A theoretical enthalpy of formation of a molecule M at 0 K can be calculated as the difference between the summed experimental enthalpies of formation of the atoms contained in the molecule at 0 K, $\sum_{i}^{N} \Delta_{\mathrm{f}} H_{0\,\mathrm{K}}^{0}(A_i)$, and the theoretical atomization energy $TAE_{0\,K}(M)$ of the molecule.

The superscript "0" refers to 1 atm standard state. For each molecule:

$$\Delta_f H_{0\,K}^{0,TA14}(M) = \sum_i^N \Delta_f H_{0\,K}^{0,Expt}(A_i) - TAE_{0\,K}^{TA14}(M) \quad (13)$$

A theoretical enthalpy of formation at 298 K was obtained by applying the following formula:

$$\Delta_f H_{298\,K}^{0,TA14}(M) = \Delta_f H_{0\,K}^{0,TA14}(M) + \Delta\Delta H_{thermal}^{TA14}(M) - \sum_i^N [H_{298\,K}(A_i) - H_{0\,K}(A_i)]^{0,Expt} - ZPVE^{TA14}(M) \quad (14)$$

where $\Delta\Delta H_{thermal}^{TA14}(M)$ is the computed thermal correction to the enthalpy for the molecule M obtained from computed vibrational frequencies, and $[H_{298\,K}(A_i) - H_{0\,K}(A_i)]^{0,Expt}$ is the experimental integrated heat capacity for each atom A_i at its standard state. The experimental atomic enthalpy corrections and the integrated heat capacity values for each element are taken from the CODATA thermochemical database (Table 2).[73] In eqn (14), computed zero-point vibrational energy contributions (already included in the total atomization energies) were subtracted from enthalpies of formation of the molecule at 0 K to avoid their double-counting.

We computed the Gibbs free energy of formation of each molecule as follows. We combined the computed entropy of formation, $\Delta_f S_{298\,K}^{0,TA14}(M)$, to the gas phase enthalpy of formation:

$$\Delta_f G_{298\,K}^{0,TA14}(M) = \Delta_f H_{298\,K}^{0,TA14}(M) - T\Delta_f S_{298\,K}^{0,TA14}(M) \quad (15)$$

where $\Delta_f S_{298\,K}^{0,TA14}(M)$ was calculated as follows:

$$\Delta_f S_{298\,K}^{0,TA14}(M) = S_{298\,K}^{TA14}(M) - \sum_i^N \nu_i S_{298\,K}^{0,Expt}(D_i) \quad (16)$$

For all polyatomic molecules, $S_{298\,K}^{TA14}(M)$ comprises computed anharmonic vibrational, rotational, and translational contributions to the molecular entropy at 298 K. For the diatomic molecules, the anharmonic contribution to vibrations was taken from experimental data, as discussed above. $S_{298\,K}^{0,Expt}(D_i)$ is the experimental entropy for each diatomic element at its standard state, as taken from the CODATA thermochemical database (Table 2),[73] and ν_i is the appropriate stoichiometric coefficient. For example, the $\Delta_f S_{298\,K}^{0,TA14}$ value of HOBr is:

$$\Delta_f S_{298\,K}^{0,TA14}(HOBr) = S_{298\,K}^{TA14}(HOBr) - \frac{S_{298\,K}^{0,Expt}(H_2)}{2} - \frac{S_{298\,K}^{0,Expt}(O_2)}{2} - \frac{S_{298\,K}^{0,Expt}(Br_2)}{2} \quad (17)$$

The resulting $\Delta_f H_{298\,K}^{0,TA14}(M)$ and $\Delta_f G_{298\,K}^{0,TA14}(M)$ values are thus based on a combination of experimental data (*e.g.*, $\Delta_f H_{0\,K}^{0,Expt}(A_i)$, $[H_{298\,K}(A_i) - H_{0\,K}(A_i)]^{0,Expt}$, and $S_{298\,K}^{0,Expt}(A_i)$) and computational results ($TAE_{0\,K}^{TA14}(M)$, $\Delta\Delta H_{thermal}^{TA14}(M)$, and $S_{298\,K}^{0,TA14}(M)$), but they are considered as theoretical values.

2.6 Diagnostics for nondynamical correlation effects

Diagnostics for nondynamical correlation (NDC) effects provide an indication of the importance of post-CCSD(T) electronic contributions for thermochemical applications. Among several proposed diagnostics, the %TAE[HF] is the most affordable *a priori* energy-based diagnostic, and %TAE[(T)] is a more reliable indicator that also requires no post-CCSD(T) calculations.[61] %TAE[post-CCSD(T)] is an *a posteriori* diagnostic to evaluate the post-CCSD(T) contributions to total atomization energy.[61] These diagnostics are calculated as follows:

$$\%TAE[HF] = 100 \times \frac{TAE_e(HF)}{TAE_e(CCSD(T))} \quad (18)$$

$$\%TAE[(T)] = 100 \times \frac{TAE_e(CCSD(T)) - TAE_e(CCSD)}{TAE_e(CCSD(T))} \quad (19)$$

$$\%TAE[post\text{-}CCSD(T)] = 100 \times \frac{TAE_e(post\text{-}CCSD(T)) - TAE_e(CCSD(T))}{TAE_e(post\text{-}CCSD(T))} \quad (20)$$

where $TAE_e(HF)$, $TAE_e(CCSD)$ and $TAE_e(CCSD(T))$ represent the non-relativistic HF, CCSD, and CCSD(T) atomization energy components at the bottom of the well. $TAE_e(post\text{-}CCSD(T))$ contains the non-relativistic higher excitation energy contributions T–(T), (Q), and Q–(Q), but excludes core–valence and relativistic contributions.

3 Results and discussion

We computed total atomization energies at 0 K, standard heats of formation at 0 K and at 298 K, and Gibbs free energies of formation at 298 K for bromamines, chloramines, bromochloramines, and other related molecules. First, we report total atomization energy data and discuss the electronic energy contributions to bond formation in these molecules. This is followed by a discussion of diagnostics for nondynamical correlation. Then, to assess the performance of the TA14 approach, we compare our computed property data to experimental data and other published benchmarks, where available. Finally we briefly discuss the implications of thermochemistry data for halamines.

Table 2 Experimental atomic enthalpies of formation $\Delta_f H_{0\,K}^{0,Expt}(A_i)$, integrated atomic heat capacities $[H_{298\,K}(A_i) - H_{0\,K}(A_i)]^{0,Expt}$ (kcal mol^{-1}), and entropies (cal mol^{-1} K^{-1}) for selected diatomic molecules at 298 K at their standard state

Element A_i	Reference state	$\Delta_f H_{0\,K}^{0,Expt}(A_i)$	$[H_{298\,K}(A_i) - H_{0\,K}(A_i)]^{0,Expt}$	$S_{298\,K}^{0,Expt}(D_i)$
H	$H_{2,gas}$	51.6336 ± 0.0014	1.012 ± 0.000	31.2333 ± 0.0007
N	$N_{2,gas}$	112.5287 ± 0.0956	1.036 ± 0.000	45.7957 ± 0.0010
O	$O_{2,gas}$	58.9842 ± 0.0239	1.037 ± 0.000	49.0325 ± 0.0012
Cl	$Cl_{2,gas}$	28.5901 ± 0.0019	1.097 ± 0.000	53.3176 ± 0.0024
Br	$Br_{2,liq}$	28.1836 ± 0.0287	2.930 ± 0.001	36.38

3.1 Total atomization energies

Benchmark-level total atomization energies were obtained with the TA14 method, taking into account our best estimate CCSD(T) and post-CCSD(T) contributions, core–valence electronic correlation, relativistic effects and DBOC contributions. The component breakdown of the total atomization energies at the bottom of the potential energy well, TAE_e, and at 0 K, $TAE_{0\,K}$, is displayed in Table 3 for both chemical sets A and B.

Electron correlation is a substantial contributor to the bond formation of chloramines and bromamines. For the monohalogenated species, the $\Delta E_{CCSD,Extrap}$ and $\Delta E_{(T),Extrap}$ energy components together explain >40% of the TAE_e. For the dihalogenated and trihalogenated species, the combined $\Delta E_{CCSD,Extrap}$ and $\Delta E_{(T),Extrap}$ contributions dominate over the $E_{HF,Extrap}$ energy component altogether. The $E_{HF,Extrap}$ component dwindles progressively with increasing halogenation. The chloramines and bromamines are thus relatively weakly bound molecules, held together largely by electron correlation forces, and presumably this accounts for their high reactivity.

For both NBr_3 and NBr_2Cl, the $E_{HF,Extrap}$ component of the TAE_e is actually less than zero, indicating that these molecules are not predicted to be stable at the Hartree–Fock level. In other words, electronic correlation effects are entirely responsible for their stable formation. This is an unusual situation; a few other species have been reported to exhibit negative or near-zero Hartree–Fock contributions to the TAE_e, and many of them are halogen-containing molecules: O_3, MgO, $BN(^1\Sigma^+)$, F_2, FO_2, F_2O_2, FO, F_2O, OClO, and ClOO are characterized by negative or near-zero Hartree–Fock atomization energies, and their stable formation is thus explained entirely by dynamical and non-dynamical electron correlation effects.[61,135] Dynamical and nondynamical correlation contributions are discussed further in the next section.

Post-CCSD(T) contributions to electronic correlation energies are varied. For example, $\Delta E_{T-(T),Extrap}$, $\Delta E_{(Q)}$, and $\Delta E_{Q-(Q)}$ contributions together account for −0.49 kcal mol^{-1} of the total atomization energy of NBr_2Cl. However for most of the halamines, the $\Delta E_{T-(T),Extrap}$, $\Delta E_{(Q)}$, and $\Delta E_{Q-(Q)}$ components tend to cancel each other. The $\Delta E_{T-(T),Extrap}$ energy components are destabilizing in all cases (<0), whereas the quadruple excitation contributions are uniformly stabilizing (>0). This is consistent with the trends in post-CCSD(T) components found previously for other small molecules.[60,61,114]

Core–valence electronic correlation contributions to the total atomization energy are non-negligible for bromamines and chloramines. The ΔE_{CORE} values reported for chloramines range from 0.62 kcal mol^{-1} to 0.74 kcal mol^{-1}. For bromamines and bromochloramines, values range from 0.66 kcal mol^{-1} ($NBrCl_2$) to 3.24 kcal mol^{-1} (NBr_3). Core–valence electronic correlation contributions thus have critical importance in achieving benchmark accuracy in the TAE.

Relativistic energy components also have an important role for estimating thermochemical properties of these molecules. The ΔE_{REL} and $\Delta E_{2nd\,SO}$ components contribute quantitatively to the total atomization energies of halamines. The scalar relativistic effects, ΔE_{REL}, of halamines are negative with values

Table 3 Component breakdown of the best estimate total atomization energies at the bottom of the well (TAE_e) and at 0 K ($TAE_{0\,K}$) [kcal mol^{-1}]

	HF[a]	CCSD[b]	(T)[b]	T–(T)[b]	(Q)	Q–(Q)	Core shell[b]	Scalar relat.	1st order spin–orbit	2nd order spin–orbit	DBOC	TAE_e	ZPVE	$TAE_{0\,K}$
Set A														
H_2	83.85	25.67	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.02	109.54	6.21[c]	103.34
N_2	115.42	102.22	9.46	−0.75	1.08	−0.15	1.07	−0.14	0.00	0.00	0.00	228.20	3.33[c]	224.87
O_2	18.77	91.70	9.24	−0.42	1.08	−0.12	0.45	−0.18	−0.45	0.00	0.00	120.07	2.19[c]	117.88
Cl_2	19.23	35.65	4.79	−0.44	0.43	−0.02	0.22	−0.18	−1.68	−0.09	0.00	57.91	0.79[c]	57.12
Br_2	16.09	32.08	4.17	−0.32	0.35	−0.02	0.54	−0.36	−7.02	0.40	0.00	45.91	0.47[c]	45.44
HCl	77.08	28.75	1.60	−0.14	0.09	0.00	0.25	−0.24	−0.84	−0.05	0.03	106.51	4.17[c]	102.32
HBr	65.12	26.93	1.40	−0.08	0.08	0.00	0.57	−0.49	−3.51	0.19	0.02	90.23	3.75[c]	86.48
HOCl	78.82	80.11	6.93	−0.50	0.59	0.05	0.40	−0.31	−1.06	−0.05	0.03	165.01	7.92	157.09
HOBr	76.75	79.30	6.75	−0.46	0.59	−0.07	0.39	−0.65	−3.73	0.20	0.04	159.10	7.91	151.19
H_2O	155.92	73.14	3.59	−0.23	0.19	−0.02	0.48	−0.26	−0.22	0.00	0.09	232.67	13.22	219.454
NH_3	201.12	92.28	3.92	−0.15	0.02	−0.02	0.79	−0.24	0.00	0.00	0.09	297.81	21.20	276.61
Set B														
NH_2Cl	142.01	98.49	6.95	−0.46	0.47	−0.04	0.74	−0.38	−0.84	−0.05	0.05	246.95	16.30	230.65
$NHCl_2$	79.84	107.66	10.92	−0.89	0.93	−0.09	0.70	−0.39	−1.68	−0.09	0.02	196.92	10.45	186.48
NCl_3	13.78	119.64	15.92	−1.46	1.58	−0.20	0.62	−0.29	−2.52	−0.14	0.01	146.45	3.84	143.11
NH_2Br	135.81	97.75	6.85	−0.41	0.48	−0.04	0.92	−0.63	−3.51	0.20	0.05	237.46	15.93	221.53
$NHBr_2$	66.13	106.55	10.76	−0.81[d]	0.97	−0.11	1.11	−0.54	−7.02	0.40	0.02	177.44	9.81	167.64
NBr_3	−7.29	118.63	15.93	−1.39[d]	1.29[e]	N/A[f]	3.24[g]	−0.14	−10.54	0.61	0.01	120.34	2.98	117.36
NHBrCl	73.51	107.14	10.87	−0.83[d]	0.95	−0.10	1.22[h]	−0.45	−4.35	0.15	0.02	188.12	10.13	177.99
$NBrCl_2$	5.04	120.29	16.41	−1.41[d]	1.74	−0.24	0.66	−0.20	−5.19	0.11	0.01	137.21	3.56	133.65
NBr_2Cl	−0.58	119.12	16.01	−1.67[d]	1.22[e]	−0.04	2.58[g]	−0.15	−7.86	0.36	0.01	129.00	3.27	125.72

[a] Hartree–Fock energies extrapolated using eqn (7). [b] Correlation energies extrapolated using eqn (8). [c] For diatomic molecules, harmonic zero-point vibrational energy values were computed, and experimental anharmonicity contributions were added to these values. [d] For $NBrCl_2$, NBr_2Cl, $NHBr_2$, NHBrCl and NBr_3 this contribution is computed with the pV(D,T)Z basis set pair. [e] For NBr_2Cl and NBr_3 this contribution is computed with the pVDZ basis set. [f] Not available. [g] For NBr_2Cl and NBr_3 this contribution is computed with the AWCVTZ basis set, and no extrapolation to the complete basis set limit was applied. [h] For NHBrCl this contribution is computed with the AWCVQZ basis set, and no extrapolation to the complete basis set limit was applied.

that range from −0.14 kcal mol^{-1} (NBr_3) to −0.63 kcal mol^{-1} (NH_2Br). $\Delta E_{2nd\,SO}$ values range from −0.14 kcal mol^{-1} (NCl_3) to 0.61 kcal mol^{-1} (NBr_3). These energy contributions, although small, have to be considered to achieve the desired accuracy in TAE calculations. The $\Delta E_{1st\,SO}$ contribution is simply an additive function of the elemental composition of the molecule and therefore it is not discussed.

Finally, ΔE_{DBOC} components are the smallest energy contributions considered. Among the halamines, the largest values are 0.05 kcal mol^{-1} found for NH_2Cl and NH_2Br.

3.2 Importance of nondynamical correlation for halamines

Nondynamical electron correlation (NDC) contributes substantially to the electronic structure of chloramines and bromamines, and this merits a brief discussion. The nondynamical electronic correlation refers to the interelectronic interactions for those systems where the reference configuration (defined as the HF wavefunction) is affected by quasidegeneracy and is not well-described by a single predominating configuration.[136] Chloramines and bromamines all exhibit nondynamical correlation (Table 4). This effect becomes increasingly important with increasing number of halogen atoms in the molecule. The wavefunctions of all four trihalamine species are dominated by multireference character as diagnosed by very low %TAE[HF] values and high %TAE[(T)] values. Monohalamines and dihalamines exhibit mild to moderate levels of nondynamical correlation.

These NDC diagnostics provide a rough indication of the reliability of single-reference approaches in the evaluation of the electronic structure. In order to provide a more detailed description of systems dominated by NDC, a multireference electronic structure method is generally required. However, the electronic energies of such systems can be quantitatively recovered with high-order coupled cluster methods based on a single-determinant HF reference.[61,66,71]

3.3 Comparison of computed $TAE_{0\,K}$ values with previous experimental and theoretical data

Our best estimate total atomization energies at 0 K, $TAE^{TA14}_{0\,K,\text{“Best”}}$, are in excellent agreement with previously published experimental values, where available. For all species in set A there is agreement to within 0.23 kcal mol^{-1} or less (Table 5). The average absolute deviation from experiments is 0.10 kcal mol^{-1}. The largest disagreement from experiment is for HOCl (0.23 kcal mol^{-1}), followed by HBr with a deviation of −0.14 kcal mol^{-1}. These results indicate that the *ab initio* protocol employed here has achieved $\leq$1 kJ mol^{-1} accuracy for the small molecules of set A. This is consistent with previous high-level *ab initio* work using comparable methodologies.[61,63]

Our $TAE^{TA14}_{0\,K,\text{“Best”}}$ results are also in very good agreement with previous theoretical values from W4 ($TAE^{W4}_{0\,K}$) and FPD calculations ($TAE^{FPD}_{0\,K}$), where comparisons can be made. $TAE^{TA14}_{0\,K,\text{“Best”}}$ and $TAE^{W4}_{0\,K}$ agree to within 0.11 kcal mol^{-1} for monochloramine. For molecule set A, the highest discrepancies between $TAE^{TA14}_{0\,K,\text{“Best”}}$ and $TAE^{W4}_{0\,K}$ are found for N_2 (−0.14 kcal mol^{-1}) and HOCl (0.37 kcal mol^{-1}). These differences can be explained chiefly by a few energy contributions that were computed differently. First, Karton *et al.* employed a different definition of frozen-core electrons from that implemented in CFOUR, and, as a consequence, the estimates of the core–valence contributions differ by 0.14 kcal mol^{-1} for HOCl. Second, the W4 estimate of the zero-point vibrational energy of HOCl was 8.18 kcal mol^{-1}, taken from theoretical data[137] calculated at the MRCI/AV(D,T,Q)Z level, and this differs from our VPT2-B2PLYPD/AVQZ value (7.92 kcal mol^{-1}) and from the experimental value of 7.97 kcal mol^{-1}.[138–140]

Table 4 Diagnostics for nondynamical correlation (NDC)

Compound	%TAE[HF]	%TAE[(T)]	%TAE[post-CCSD(T)]	NDC evaluation based on %TAE[(T)][a]
N_2	50.9	4.16	0.076	Mild NDC
O_2	15.7	7.72	0.443	Moderate NDC
Cl_2	32.4	8.03	−0.051	Moderate NDC
Br_2	30.9	7.97	0.035	Moderate NDC
HCl	71.8	1.49	0.048	Mild NDC
HBr	69.7	1.50	−0.006	Mild NDC
HOCl	47.6	4.18	0.084	Mild NDC
HOBr	47.2	4.14	0.037	Mild NDC
H_2O	67.1	1.54	−0.029	Mild NDC
NH_3	67.7	1.32	−0.048	Mild NDC
NH_2Cl	57.4	2.81	−0.012	Mild NDC
$NHCl_2$	40.3	5.50	−0.031	Moderate NDC
NCl_3	9.3	10.66	−0.049	Severe NDC
NH_2Br	56.5	2.85	0.010	Mild NDC
$NHBr_2$	36.1	5.86	0.022	Moderate NDC
NBr_3	−5.8	12.52	−0.080	Severe NDC
NHBrCl	38.5	5.68	0.008	Moderate NDC
$NBrCl_2$	3.6	11.58	0.065	Severe NDC
NBr_2Cl	−0.4	11.90	−0.364	Severe NDC

[a] Following the qualitative interpretation proposed by Karton *et al.*,[61,65] systems are dominated by dynamic correlation when the %TAE[(T)] value is below 2%, whereas a large nondynamical correlation contribution is indicated by a %TAE[(T)] value greater than 10%. %TAE[(T)] between 2% and 4–5% and between 4–5% and 10% suggest mild and moderate levels of nondynamical correlation, respectively. %TAE[HF] is a more generic and lower-cost predictor for NDC: a %TAE[HF] value above 66.7% indicates a system not affected by NDC, whereas a %TAE[HF] below 20% indicates a molecule dominated by a severe nondynamical correlation.

Table 5 Total atomization energies at 0 K: experimental and theoretical values [kcal mol^{-1}]

Compound	$TAE_{0\,K,\text{"Best"}}^{TA14}$	$TAE_{0\,K,\text{"Halkier"}}^{TA14}$	$TAE_{0\,K}^{W4}$ [60,61]	$TAE_{0\,K}^{FPD}$ [63]	$TAE_{0\,K}^{Expt}$
Set A					
H_2	103.34	103.36	103.29	103.27 ± 0.02	103.27[77]
N_2	224.87	224.93	225.01	224.88 ± 0.3	224.94 ± 0.01[61]
O_2	117.88	117.88	117.88	117.92 ± 0.2	117.99 ± 0.00[61]
Cl_2	57.12	57.81	57.03	57.23 ± 0.3	57.18 ± 0.00[61]
Br_2	45.44	45.50	N/A[d]	45.39 ± 0.3	45.46 ± 0.07[77]
HCl	102.32	102.59	102.23	102.15 ± 0.2	102.21 ± 0.00[61]
HBr	86.48	86.48	N/A[d]	86.47 ± 0.2	86.62 ± 0.05[77]
HOCl	157.09	157.53	156.72	156.94 ± 0.4	156.86 ± 0.03[c]
HOBr	151.19	151.23	N/A[d]	N/A[d]	151.28 ± 0.21[c]
H_2O	219.45	219.46	219.36	219.38 ± 0.2	219.36 ± 0.01[61]
NH_3	276.61	276.66	276.60	276.48 ± 0.3	276.59 ± 0.01[61]
Average absolute deviation$_1$[a]	**0.09**	**0.22**		**0.06**	
Average absolute deviation$_2$[b]	**0.10**	**0.28**	**0.06**	**0.06**	
Average deviation$_1$[a]	**0.00**	**0.18**		**−0.03**	
Average deviation$_2$[b]	**0.03**	**0.25**	**−0.04**	**−0.02**	
Signed maximum deviation[a]	**0.23** (HOCl)	**0.67** (HOCl)	**−0.15** (Cl_2)	**−0.15** (HBr)	
Set B					
NH_2Cl	230.65	231.03	230.54	N/A[d]	N/A[d]
$NHCl_2$	186.48	187.20	N/A[d]	N/A[d]	N/A[d]
NCl_3	143.11	144.16	N/A[d]	N/A[d]	N/A[d]
NH_2Br	221.53	221.58	N/A[d]	N/A[d]	N/A[d]
$NHBr_2$	167.64	167.70	N/A[d]	N/A[d]	N/A[d]
NBr_3	117.36	117.49	N/A[d]	N/A[d]	N/A[d]
NHBrCl	177.99	178.38	N/A[d]	N/A[d]	N/A[d]
$NBrCl_2$	133.65	134.34	N/A[d]	N/A[d]	N/A[d]
NBr_2Cl	125.72	126.15	N/A[d]	N/A[d]	N/A[d]

[a] The deviations were calculated considering all available experimental data. [b] Only the compounds studied by Karton *et al.* are considered. [c] Reference $TAE_{0\,K}$ for HOCl and HOBr are calculated from experimental molecular $\Delta_f H^0_{0\,K}$ and experimental atomic heat capacities. [d] Not available.

For N_2, discrepancies between the two theoretical methods are likely due to slightly different calculations of post-CCSD(T) contributions. In the W4 protocol, the quadruple excitation energies are calculated as 1.10[(CCSDTQ-CCSDT(Q)) + (CCSDT(Q)-CCSDT)], whereas our estimates are calculated without the empirical scalar factor 1.10. Furthermore, CCSDTQ5 contributions were not included in our protocol. These dissimilarities between our method and W4 produce a discrepancy in the post-CCSD(T) energy value of N_2. Finally, for molecule set A, the largest discrepancies between $TAE_{0\,K,\text{"Best"}}^{TA14}$ and $TAE_{0\,K}^{FPD}$ are for HCl and HOCl (0.17 and 0.15 kcal mol^{-1}, respectively). In summary, TA14 exhibits excellent agreement with W4 for monochloramine and excellent agreement with W4 and FPD values for molecules of set A, providing further confirmation that TA14 produces sub-kJ mol^{-1} accuracy for atomization energies of small molecules containing atoms up to the third row. Based on comparisons between TA14 and these other theoretical methods, we conclude that the predominating sources of uncertainties in our $TAE_{0\,K}$ values are in the calculations of the core–valence electron correlation energies and post-CCSD(T) energy treatments.

Based on the above comparisons to experimental and previous theoretical data, we conclude that our best TA14 computations have 1 kJ mol^{-1} (0.24 kcal mol^{-1}) uncertainty in the $TAE_{0\,K}$ for the chloramines (NH_2Cl, $NHCl_2$, and NCl_3) and for monobromamine (NH_2Br). We conservatively assign larger uncertainties of 3 kJ mol^{-1} (0.72 kcal mol^{-1}) for the $TAE_{0\,K}$ values of $NHBr_2$, NBr_3, NHBrCl, $NBrCl_2$, and NBr_2Cl, which exhibit larger core–valence correlation and post-CCSD(T) energy contributions, and for which we were required to apply slightly lower levels of theoretical treatment.

For purposes of further comparisons, we additionally employed the Halkier extrapolation formula (eqn (9)) for the computations of Hartree–Fock and correlation energies. We compared these data with results obtained following our "Best" TA14 approach, which employs W4 extrapolation formulae (eqn (7) and (8)), as shown in Table 5. The $TAE_{0\,K,\text{"Halkier"}}^{TA14}$ values exhibit higher deviations with respect to experiments, with an average absolute deviation of 0.28 kcal mol^{-1} in the $TAE_{0\,K}$. The largest disagreement is found for HOCl, which differs from the experimental data by 0.67 kcal mol^{-1} using the Halkier extrapolation. Consistent with previous work,[61,71] we find that eqn (7) and (8) perform better than the Halkier's extrapolation formula for total atomization energies, with the large basis sets employed here.

3.4 Gas phase enthalpies of formation at 0 K and at 298 K

Our computed gas phase enthalpies of formation at 0 K, $\Delta_f H^{0,TA14}_{0\,K,\text{"Best"}}$, are in excellent agreement with experimental data for molecule set A. Our best calculated values at 0 K exhibit an average absolute deviation of 0.11 kcal mol^{-1} from experiment, indicating that the TA14 method achieves confident kJ mol^{-1} accuracy in the $\Delta_f H^0_{0\,K}$ for these systems. The computed enthalpy of formation at 0 K of HOCl is the most inaccurate, with a deviation of −0.23 kcal mol^{-1} from experiment and a discrepancy of 0.37 kcal mol^{-1} with respect to the W4.2 value (−17.51 ± 0.14 kcal mol^{-1}).[65] This discrepancy from the W4.2 result arises from electronic and vibration contributions

Table 6 Gas phase enthalpies of formation at 0 K: experimental and theoretical values [kcal mol^{-1}]

Compound	$\Delta_f H^{0,TA14}_{0\,K,\text{"Best"}}$	$\Delta_f H^{0,W4.2}_{0\,K}$	$\Delta_f H^{0,Expt}_{0\,K}$
Set A			
H_2	−0.07	N/A[a]	0.00[73–75]
N_2	0.19	N/A[a]	0.00[73–75]
O_2	0.09	N/A[a]	0.00[73–75]
Cl_2	0.06	N/A[a]	0.00[73–75]
Br_2	10.93	N/A[a]	10.92 ± 0.03[73]
HCl	−22.10	N/A[a]	−22.02 ± 0.02[73]
HBr	−6.66	N/A[a]	−6.80 ± 0.04[73]
HOCl	−17.88	−17.51 ± 0.14[65]	−17.654 ± 0.007[74,75]
HOBr	−12.38	N/A[a]	−12.48 ± 0.16[74,75]
H_2O	−57.20	N/A[a]	−57.10 ± 0.01[141]
NH_3	−9.18	N/A[a]	−9.31 ± 0.08[73]
Average absolute deviation	**0.11**		
Average deviation	**0.02**		
Signed maximum deviation	**−0.23** (HOCl)		
Set B			
NH_2Cl	13.74	N/A[a]	N/A[a]
$NHCl_2$	34.87	N/A[a]	N/A[a]
NCl_3	55.19	N/A[a]	N/A[a]
NH_2Br	22.45	N/A[a]	N/A[a]
$NHBr_2$	52.89	N/A[a]	N/A[a]
NBr_3	79.72	N/A[a]	N/A[a]
NHBrCl	42.95	N/A[a]	N/A[a]
$NBrCl_2$	64.24	N/A[a]	N/A[a]
NBr_2Cl	95.21	N/A[a]	N/A[a]

[a] Not available.

to the $TAE_{0\,K}$, discussed in the previous section. The computed enthalpies of formation at 0 K for HBr and N_2 are overestimated by about 0.20 kcal mol^{-1} compared to experiment. These discrepancies arise primarily from the uncertainties in the calculations of the electronic contributions to total atomization energies, as discussed in the previous section.

For molecule set A, computed gas phase enthalpies of formation at 298 K, $\Delta_f H^{0,TA14}_{298\,K,\text{"Best"}}$, also exhibit sub-kJ mol^{-1} agreement with available experimental data (Table 7). The largest deviations from experiment were found for HOCl and N_2, with differences of −0.20 and 0.18 kcal mol^{-1}, respectively. Errors in the computed gas phase enthalpy of formation are of similar magnitude at 0 K and at 298 K (Tables 6 and 7). It is worth noting that $\Delta_f H^{0,Expt}_{298\,K}$ values are probably not independent of reported $\Delta_f H^{0,Expt}_{0\,K}$ values. We did not verify whether the experimental data found in different databases, such as JANAF-Thermochemical Tables,[76] CODATA,[73] ATCT,[74,75] and CCCBDB,[77] originate from common experimental sources.

Chloramines and bromamines are found to be endothermic with respect to the elements in their standard states. $\Delta_f H^{0,TA14}_{298\,K,\text{"Best"}}$ values range from 12.04 kcal mol^{-1} to 91.00 kcal mol^{-1} for chloramines, bromamines and bromochloramines (Table 7). No experimental heat of formation data are available for the halamines. Based on comparisons of our dataset with other computed and experimental data for molecule set A, we consider that the major sources of uncertainty in the $\Delta_f H^{0,TA14}_{298\,K,\text{"Best"}}$ arise from the post-CCSD(T) electron correlation contributions to the $TAE_{0\,K}$. For the chloramines (NH_2Cl, $NHCl_2$, and NCl_3) and for monobromamine (NH_2Br), we estimate 1 kJ mol^{-1} (0.24 kcal mol^{-1}) uncertainties in the computed $\Delta_f H^0_{0\,K}$ and $\Delta_f H^0_{298\,K}$ estimates. For $NHBr_2$, NBr_3, and for the bromochloramines, we assign larger uncertainties of 3 kJ mol^{-1} (0.72 kcal mol^{-1}) in computed $\Delta_f H^0_{0\,K}$ and $\Delta_f H^0_{298\,K}$ values, for reasons discussed in the section on $TAE_{0\,K}$ data.

Recently, Rayne and Forest reported standard enthalpies of formation at 298 K for chloramines computed at the G4MP2 and G4 levels and for monobromamine and dibromamine at the G4 level (Table 7).[56,58] These protocols represent lower levels of theory than the methods employed here. The G4 and G4MP2 methods do not include any post-CCSD(T) energy calculations and do not employ basis sets larger than 6-31G(2df,p) and 6-31+G(d). Reported G4 estimates of $\Delta_f H^0_{298\,K}$ deviate from our best estimates by 0.03 to 0.98 kcal mol^{-1} for the chloramines, monobromamine, and dibromamine (Table 7). Reported G4MP2 data exhibit larger deviations from our best estimates, with a difference of 1.99 kcal mol^{-1} found for the $\Delta_f H^0_{298\,K}$ value of trichloramine. Thus our computed enthalpy of formation values substantially improve upon these previously reported estimates.

3.5 Gibbs free energies of formation at 298 K

For the molecule set A, our best estimate $\Delta_f G^{0,TA14}_{298\,K,\text{"Best"}}$ values show good agreement with experimental data, with an average absolute deviation of 0.09 kcal mol^{-1} (Table 8). The $\Delta_f G^{0,TA14}_{298\,K,\text{"Best"}}$ of HOCl exhibits the largest disagreement from experiment, with a deviation of 0.19 kcal mol^{-1}. This is consistent with the accuracy found for the computed enthalpy of formation, $\Delta_f H^{0,TA14}_{298\,K,\text{"Best"}}$. A comparison of computed and experimental $\Delta_f S^0_{298\,K}$ values revealed an average absolute error of only 0.08 cal mol^{-1} K^{-1} and a maximum unsigned deviation of 0.12 cal mol^{-1} K^{-1} (for both H_2 and Br_2). Errors in the computed entropy thus contribute less than 0.04 kcal mol^{-1} in the $\Delta_f G^0_{298\,K}$, for all molecules of set A.[77] Our computed vibrational

Table 7 Gas phase enthalpies of formation at 298 K: experimental and theoretical values [kcal mol^{-1}]

Compound	$\Delta_f H^{0,TA14}_{298\,K,\text{"Best"}}$	$\Delta_f H^{0,Comp}_{298\,K}$	$\Delta_f H^{0,Expt}_{298\,K}$
Set A			
H_2	−0.03	0.00 ± 0.02[63]	0.00[74,75]
N_2	0.18	0.2 ± 0.3[63]	0.00[74,75]
O_2	0.09	0.0 ± 0.2[63]	0.00[74,75]
Cl_2	0.06	$<0.1 \pm 0.3$[63]	0.00[74,75]
Br_2	7.38	7.4 ± 0.3[63]	7.39 ± 0.03[74–76]
HCl	−22.14	-22.0 ± 0.2[63]	-22.030 ± 0.001[74,75]
HBr	−8.54	-8.5 ± 0.2[63]	-8.61 ± 0.03[74,75]
HOCl	−18.56	-18.20 ± 0.14[65] -18.1 ± 0.3[142] -17.9 ± 0.3[58] -18.1 ± 0.4[63]	-18.357 ± 0.007[74,75]
HOBr	−14.90	-15.3 ± 0.6[142] −14.57[56]	-15.00 ± 0.16[74,75]
H_2O	−57.90	-57.8 ± 0.2[63] -57.6 ± 0.3[58]	-57.80 ± 0.01[74–76]
NH_3	−10.86	-10.7 ± 0.3[63] -10.3 ± 0.3[58]	-10.889 ± 0.007[74,75]
Average absolute deviation	**0.07**		
Average deviation	**0.03**		
Signed maximum deviation	**−0.20** (HOCl)		
Set B			
NH_2Cl	12.04	13.02[56] 12.4[58]	N/A[a]
$NHCl_2$	33.47	33.44[56] 32.5[58]	N/A[a]
NCl_3	54.36	53.56[56] 52.37[58]	N/A[a]
NH_2Br	18.97	19.90[56]	N/A[a]
$NHBr_2$	48.02	47.56[56]	N/A[a]
NBr_3	73.82	N/A[a]	N/A[a]
NHBrCl	39.80	N/A[a]	N/A[a]
$NBrCl_2$	61.72	N/A[a]	N/A[a]
NBr_2Cl	91.00	N/A[a]	N/A[a]

[a] Not available.

frequencies are in excellent agreement with experiment, exhibiting an average absolute deviation value of 4 cm^{-1}, and a maximum deviation of −58 cm^{-1} (for H_2), for set A.

For the computed $\Delta_f G^{0,TA14}_{298\,K,\text{"Best"}}$ values of set A, the most important sources of deviation from experiment were considered to be the uncertainties in the estimation of the core–valence correlation and post-CCSD(T) electronic correlation contributions to total atomization energies. These effects are discussed in previous section.

Halamine formation is endergonic with respect to the elemental forms at standard state, with $\Delta_f G^{0,TA14}_{298\,K,\text{"Best"}}$ values ranging from 19.39 kcal mol^{-1} to 93.46 kcal mol^{-1}. No experimental gas phase thermochemistry data are available for halamines. Based on results for molecule set A, we estimate 1 kJ mol^{-1} (0.24 kcal mol^{-1}) uncertainties in the computed $\Delta_f G^0_{298\,K}$ values of the chloramines (NH_2Cl, $NHCl_2$, and NCl_3) and of monobromamine (NH_2Br). For $NHBr_2$, NBr_3, and for the bromochloramines, we assign larger uncertainties of 3 kJ mol^{-1} (0.72 kcal mol^{-1}) in computed $\Delta_f G^0_{298\,K}$ values, for reasons discussed in the section on $TAE_{0\,K}$ data. It is worth noting that, unlike molecules of set A, the di- and tri-halogenated amines contain some low frequencies, with the lowest frequencies ranging from 148 cm^{-1} (NBr_3) to 283 cm^{-1} ($NHCl_2$) (see ESI†). However, the anharmonic corrections do not account for more than 5 cm^{-1} of the low-frequency bending modes of any of these species. Accurate gas phase Gibbs free energies of formation at 298 K are key thermodynamic properties for studying reaction chemistry involving halamines. This is illustrated further in the next section.

4 Implications for aqueous chemistry of chloramines and bromamines

The purpose of this study is to provide accurate thermochemistry data describing the formation of chloroamines, bromamines, and bromochloramines. With the W4 and FPD procedures as a guiding basis, we successfully designed a computational method (TA14) that accomplished this goal. It was not our aim to test TA14 against a broad thermochemical database. However, our limited assessment of molecules that are structurally related to the halamines confirms that our approach successfully achieved the targeted level of accuracy in thermochemical properties.

The estimation of gas phase free energies of formation of chloramines, bromamines, and bromochloramines allows us to predict the equilibrium constants for the reactions involving these species. By combining gas phase $\Delta_f G^{0,TA14}_{298\,K,\text{"Best"}}$ data reported here together with experimental or computed estimates of solvation free energies for the pertaining species, it is possible to assess

Table 8 Gas phase Gibbs free energies of formation at 298 K: experimental and theoretical values [kcal mol^{-1}]

Compound	$\Delta_f G^{0,TA14}_{298\,K,\text{"Best"}}$	$\Delta_f G^{0,Expt}_{298\,K}$
Set A		
H_2	−0.03	0[73]
N_2	0.18	0[73]
O_2	0.09	0[73]
Cl_2	0.06	0[73]
Br_2	0.74	0.74 ± 0.03[73]
HCl	−22.85	−22.744 ± 0.001[73]
HBr	−12.62	−12.69 ± 0.03[73]
HOCl	−15.49	−15.30 ± 0.01[73]
HOBr	−15.14	−15.26[a]
H_2O	−54.71	−54.63 ± 0.01[73]
NH_3	−3.78	−3.83 ± 0.03[73]
Average absolute deviation	**0.09**	
Average deviation	**−0.02**	
Signed maximum deviation	**0.19** (HOCl)	
Set B		
NH_2Cl	19.39	N/A[b]
$NHCl_2$	41.62	N/A[b]
NCl_3	63.38	N/A[b]
NH_2Br	22.98	N/A[b]
$NHBr_2$	49.46	N/A[b]
NBr_3	73.15	N/A[b]
NHBrCl	44.19	N/A[b]
$NBrCl_2$	67.56	N/A[b]
NBr_2Cl	93.46	N/A[b]

[a] The $\Delta_f S^{0,Expt}_{298\,K}$ value for HOBr was calculated using experimental rotational constants[143] and experimental vibrational frequencies,[144,145] assuming an *NVT* ensemble, according to statistical mechanic expressions outlined in the Hill textbook.[105] [b] Not available.

the equilibrium constants of the formation of chloramines, bromamines, and bromochloramines in aqueous phase. This can lead to further insights into the thermodynamics and the kinetics of the generation and decomposition processes affecting these reactive species during water treatment. As an illustrative example, we consider the generation of monochloramine from HOCl and NH_3 in water, which is an important reaction during water treatment:

$$NH_{3,aq} + HOCl_{aq} \overset{K_{eq,aq}}{\longleftrightarrow} NH_2Cl_{aq} + H_2O_{liq}, \quad (21)$$

where $K_{eq,aq}$ represents the aqueous equilibrium constant of the reaction shown by eqn (21). A computational estimate of $K_{eq,aq}$ can be obtained by:

$$\log K_{eq,aq} = -2.303RT \ln \Delta_{rxn}G_{aq}, \quad (22)$$

where $\Delta_{rxn}G_{aq}$ is the Gibbs free energy of reaction in aqueous phase. The $\Delta_{rxn}G_{aq}$ can be estimated from:

$$\Delta_{rxn}G_{aq} = \Delta_{rxn}G_{gas} + \Delta\Delta_{rxn}G_{solv}, \quad (23)$$

where $\Delta_{rxn}G_{gas}$ is the Gibbs free energy of reaction in gas phase and the $\Delta\Delta_{rxn}G_{solv}$ is the change in free energy of solvation upon converting reactants to products. For the reaction shown by eqn (21), $\Delta\Delta_{rxn}G_{solv}$ was deduced from available experimental Henry's law constant data for NH_3,[38] NH_2Cl,[38] and HOCl,[38] and using the value −6.31 for the ΔG_{solv} of H_2O in the 1 M standard state of the ideal dilute solution as proposed by Liptak and Shields.[146] The ΔG_{solv} for H_2O was also corrected for the conversion from the 1 M standard state to the 55.56 M pure liquid standard state, corresponding to a free energy change of 2.38 kcal mol^{-1}.[136]

Table 9 Experimental and theoretical equilibrium constants for generation of monochloramine in aqueous phase

$\Delta_{rxn}G^{TA14}_{gas}$	$\Delta\Delta_{rxn}G^{Expt}_{solv}$	$\Delta_{rxn}G^{Comp}_{aq}$	$\Delta_{rxn}G^{Expt}_{aq}$	$\log K^{Comp}_{eq,aq}$	$\log K^{Expt}_{eq,aq}$
−16.1[a]	1.8[a]	−14.3[a]	−15.6[a]	10.5	11.3

[a] kcal mol^{-1}.[1]

Using our theoretical $\Delta_f G^{0,TA14}_{298\,K,\text{"Best"}}$ data to obtain $\Delta_{rxn}G^{TA14}_{gas}$ and combining this with experimental $\Delta\Delta_{rxn}G^{Expt}_{solv}$ data, we produce a theoretical estimated equilibrium constant of $\log K^{Comp}_{eq,aq}$ = 10.5, according to eqn (22) and (23) (Table 9). For comparison, Morris and Isaac[9] proposed an experimental value of 11.3 for the equilibrium constant, $K^{Expt}_{eq,aq}$, of monochloramine generation in aqueous phase (eqn (21)), derived from the ratio of the experimental forward rate constant, k_f, with the experimental reverse rate constant, k_r:

$$\log K^{Expt}_{eq,aq} = \log \frac{k_f}{k_r} \quad (24)$$

Our theoretical $\log K^{Comp}_{eq,aq}$ is in reasonable agreement with the experimental estimate (Table 9). We suspect that the discrepancy of 1.3 kcal mol^{-1} in $\Delta_{rxn}G^{Comp}_{aq}$ arises mostly from uncertainties in the experimental Henry's law constant data used to estimate $\Delta\Delta_{rxn}G_{solv}$ or from experimental reaction rate constant data used to estimate $\Delta_{rxn}G^{Expt}_{aq}$.

Thermodynamic equilibria for hypothetical reactions of halamines with relevant species in natural water, such as inorganic anions and electron-rich organic nucleophiles, can now be determined based on free energies of formation of halamines supplied in the present study. Such reactions are relevant to understanding the chemical sinks of halamines during drinking water treatment as well as the pathways that could lead to the formation of toxic disinfection byproducts.

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