Nearly ab Initio Thermochemistry: The Use of Reaction Schemes. Application to IO and HOI

Parviz Hassanzadeh[†] **and Karl K. Irikura***[,‡]

Physical and Chemical Properties Division, National Institute of Standards and Technology,
Gaithersburg, Maryland 20899

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Reaction energetics from ab initio calculations are almost always combined with experimental data to derive enthalpies of formation. Some popular strategies are discussed, and a simple criterion is suggested for estimating the accuracy to be expected from using an arbitrary reaction. We recommend using more than one reaction scheme whenever possible and suggest how the results from different reactions may be combined in a weighted average. The uncertainties of the derived values can be estimated from the averaging procedure and by comparing the results obtained using different basis sets and treatments of electron correlation. As examples, we compute the gas-phase thermochemistry for IO^-, IO, IO^+, and HOI. As a check, analogous calculations are also done for the corresponding bromine species. Finally, we recommend that appropriate experimental data be exploited whenever they are expected to be more accurate than their theoretical counterparts. While compiling the auxiliary data to support these calculations, we found that recent measurements require that the *experimental* enthalpies of formation of many molecules be revised. We present values for HOCl, HOBr, Cl_2O, and Br_2O.

Introduction

Gas-phase thermochemistry is one of the principal applications of quantum chemistry. By definition, the standard enthalpy of formation of a gaseous molecule is the enthalpy for the balanced reaction 1, where the product is at standard pressure and temperature. In practice, reactions involving only gas-phase

$$\text{elements (standard states)} \rightarrow \text{molecule (gas)} \qquad (1)$$

species are used in calculations, and one must generally rely upon at least a limited set of auxiliary experimental data. One common choice is to compute the atomization energy of the molecule, as in reaction 2, which requires experimental values for the enthalpies of formation of the gaseous atoms. However,

$$A_nB_m\ (\text{gas}) \rightarrow nA\ (\text{gas}) + mB\ (\text{gas}) \qquad (2)$$

atomization usually changes the number of electron pairs in the system, and it has long been recognized that this leads to systematic errors in ab initio calculations.[1] A straightforward and successful attempt to correct this problem is the use of “isogyric” reactions in which the number of electron pairs, or equivalently the spin multiplicity of the system, is conserved. Adding hydrogen atoms and hydrogen molecules to any reaction, as in reaction 3, can balance the number of electron pairs while

$$C_2H_6 + 2H \rightarrow 2CH_3 + H_2 \qquad (3)$$

adding only negligibly to the computational expense.[2,3] This type of correction is an important component of the popular G2 theory for ab initio molecular energetics.[4] Alternatively, one may conserve the number of electron pairs by computing energetics for reactions that do not contain explicit bond dissociation, such as the complete hydrogenation exemplified by reaction 4.[1]

$$C_2H_6 + H_2 \rightarrow 2CH_4 \qquad (4)$$

There are other systematic problems, such as basis set superposition error[5] and vibrational zero-point energy,[6] that are not remedied by isogyric schemes. A superior approach involves “isodesmic” reactions such as reaction 5, which conserve the types of chemical bond.[7] Of course, this requires

$$C_6H_5F + CH_4 \rightarrow C_6H_6 + CH_3F \qquad (5)$$

that the corresponding auxiliary thermochemical data be available. In many cases such data are lacking, and one must rely upon the chemical similarities among elements of the same group in the periodic table for partial cancellation of systematic errors. This approach, employing *congeneric reactions*, was necessary for the examples shown below. When using such schemes, beware that chemical similarities are best among the heavier elements and that the second-period elements (Li−F) have markedly different chemistry from their congeners.[8]

The difficulties and strategies listed above have been addressed by many authors. Unfortunately, very few have given serious consideration to estimating the uncertainty associated with any specific prediction; the only serious attempt appears to be associated with Melius’ BAC-MP4 procedure.[9] For example, the uncertainties associated with the deservedly popular G2 and G2(MP2) methods are 10 and 13 kJ/mol, respectively, if it is inferred that the authors of the methods favor a value that is twice the mean absolute deviation from experimental results for a set of small molecules.[10] It is not stated whether these uncertainties are intended to represent 1σ, 2σ, or something else. Moreover, such a generic uncertainty fails to identify problem molecules for which the results are significantly worse (or better), such as SO_2[10] and SF_6.[11] Since it is well-known that some molecules are especially “difficult” for electronic structure theory, it is unlikely that meaningful uncertainties can be developed for any method without incorporating information specific to each molecule. Reliable uncertainties may not be needed in some contexts, but they are essential in most laboratory and engineering applications.

[†] E-mail: parviz.hassanzadeh@nist.gov.

[‡] E-mail: karl.irikura@nist.gov.

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TABLE 1: Experimental[a] Bond Lengths (Å), Harmonic Vibrational Frequencies (cm^{-1}), Anharmonicity Constants (cm^{-1}), Vibrational Zero-Point Energies (cm^{-1}), and Enthalpies of Formation (kJ/mol) Used in the Present Calculations and the *ab Initio* Total Energies (hartree[b]) Calculated at the CCSD(T)/6-311+G(3df,2p) Level (All Electrons Correlated)

	r_e	ω_e	$\omega_e x_e$	ZPVE	$\Delta_f H°_0$	energy
ICl	2.320878(10)	384.293(10)	1.501	191.77	19.026(40)	−7377.414 426
IO^-	1.929(10)	581(25)	4.37	289		−6992.747 052
I^-					−187.991(40)	−6917.692 809
IBr	2.468989(10)	268.640(10)	0.8140(10)	134.12	49.75(14)	−9490.587 376
BrCl	2.136065(10)	444.276(10)	1.843(10)	221.68	22.23(16)	−3032.773 015
BrO^-	1.814(9)	575(25)	4.74	286	−93.6(24)	−2648.100 468
Br^-					−206.69(23)	−2573.058 421
Br_2	2.2810(10)	325.321	1.0774	162.39	45.71(11)	−5145.948 064
Cl_2	1.9879(10)	559.72(10)	2.675(10)	279.19	0	−919.595 919
ClO^-	1.673(8)	665(25)	3.36	332	−118.6(6)	−534.923 474
Cl^-					−228.96(1)	−459.882 146
HOCl[c,d]	0.9643(5) Å	3794.1	−85.5; −26.1	2870.	−71.8(12)[e]	−535.502 598
	1.6891(2) Å	1271.6	−1.93; −7.64			
	102.96(8)°	742.5	−7.85; −6.63			
HOBr[f]	0.961 Å	3791.9	−82.6; −25.0	2777.	−50.0(11)[g]	−2648.678 954
	1.834 Å	1194.2	1.22; −7.72			
	102.3°	629.7	−7.35; −3.18			
HOI[h]	0.9643 Å[i]	[3625.8][j]	$x_{11} = -82.8$	2710[k]		−6993.321 627
	1.991 Å	[1068]				
	105.4°	[575]				

[a] Bond lengths and spectroscopic constants are from refs 21 and 20 and enthalpies of formation are from ref 34 unless otherwise noted. [b] I hartree = 2625.5 kJ/mol. [c] Equilibrium structure from ref 66. [d] Vibrational constants from ref 67. [e] Re-evaluated, see text and ref 35. [f] Approximate equilibrium structure from ref 68; vibrational constants derived from transitions predicted for $HO^{79}Br$ in ref 69. [g] Re-evaluated; see text. [h] Approximate r_0 structure and vibrational constants from ref 70. [i] Constrained to this value in ref 70. [j] Brackets denote vibrational fundamentals. [k] Approximated as ZPVE $\approx {}^1/_2(\sum \nu_i) - {}^3/_4(x_{11} + x_{22}) - {}^1/_4(x_{12} + x_{23})$, with x_{11} from ref 70 and the other anharmonicity constants from the HOBr molecule.

We present here an approach for using ab initio energetics to predict molecular enthalpies of formation along with their associated uncertainties. In particular, we suggest (1) a weighting procedure to average the results obtained using different reaction schemes and different basis sets and (2) a means for estimating the resulting accuracy on the basis of the correlation effects observed. We choose as examples the thermochemistry of IO^-, IO, IO^+, and HOI and provide results for the better-characterized bromine analogues for comparison. These molecules were chosen for their importance in tropospheric and stratospheric chemistry.[12−16]

Computational Methods, Uncertainties, and Auxiliary Data

Electronic Structure Calculations. All calculations were performed using the ACES II program suite[17,18] running on Cray YMP and IBM RS-6000/590 computers.[19] Where the data were available, experimental bond distances (r_e) were used and the total energy for each molecular species was corrected by the experimental zero-point vibrational energy (ZPVE) as listed in Table 1.[20,21] For diatomic molecules, ZPVE = $\omega_e/2 - (\omega_e x_e)/4$. For polyatomic molecules, ZPVE = ${}^1/_2\sum_i \omega_i + {}^1/_4 \sum_j \sum_{i \le j} x_{ij}$.

The segmented 6-311+G(3df,2p) basis sets for H, O, and Cl and 6-311++G(,2p) basis for H were used as supplied with the Gaussian-92/DFT program.[22] For Br and I, we used the basis sets developed by Radom and co-workers[23,24] for Gaussian-2 (G2)[4] energy calculations but split the outermost single d function into three (ratio between successive exponents = 4). These sets are contracted as (16,14,8,1)/[9,8,5,1] for Br and (16,13,9,1)/[11,10,7,1] for I. We also denote these basis sets as 6-311+G(3df). Since many of our calculations involve negative ions, we further augmented the O, Cl, Br, and I basis sets by splitting the most diffuse single s, p, and d functions into two (ratio between successive exponents = 4). These expanded basis sets include 1 + 3 + 5 = 9 additional functions and are denoted 6-311+2G(3df). When used together with the 6-311++G(,2p) basis for hydrogen, we denote the molecular basis 6-311+2+G(3df,2p). No linear-dependency problems were encountered in any of the calculations.

Sadlej's generally-contracted polarized basis sets (PBSs) for O,[25] Cl,[26] Br,[27] and I[28] were used as supplied with the ACES II program.[17,18] These medium-sized polarized basis sets were designed for correlated calculations of molecular dipole moments and dipole polarizabilities rather than for energetics. The O and Cl basis sets were slightly modified; the most diffuse contracted d-type function was decontracted, and an additional f-type function was added (α_f(O) = 1.334 and α_f(Cl) = 0.705 015). The final basis sets are thus (10,6,4,1)/[5,3,3,1] for O and (14,10,4,1)/[7,5,3,1] for Cl.

The seven-valence-electron effective core potentials (ECPs) of Wadt and Hay were also used for Br and I.[29] Corresponding valence basis sets were constructed from the uncontracted basis sets of Wadt and Hay[29] and augmented by d (ratio between successive exponents = 4) and f polarization and by s and p diffuse functions as recommended by Glukhovtsev et al.[24] These are contracted as (4,4,3,1)/[4,4,3,1] for both bromine and iodine. In the ECP series of calculations the 6-311+G(3df) basis sets were used for oxygen and chlorine.

Reaction energies are reported at the HF, MP2, CCSD, and CCSD(T) levels. The correlated calculations were done with all electrons active and also with two slightly different frozen-core approximations. In one series of energy calculations, the frozen orbitals were O (1s), Cl (1s, 2s, 2p), Br (1s, 2s, 2p, 3s, 3p), and I (1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p). In another series of calculations, the Br 3d and I 4d orbitals were also frozen.

The ion convention is used here for ion thermochemistry above 0 K.[30] This is emphasized by the symbol $\Delta_f H$ instead of $\Delta_f H°$ where appropriate.[30] These two quantities are related by $\Delta_f H° - \Delta_f H = 2.5qRT$, where q is the charge on the ion. For a singly-charged anion at 298.15 K, the difference $2.5qRT = -6.197$ kJ/mol.

Choice of Reaction Schemes. Since the bonding is similar in homologous molecules (such as ClO^- and IO^-), errors in the corresponding ab initio calculations are expected to be similar. Thus, the use of congeneric reactions causes some cancellation of systematic error. One potential source of error is spin−orbit coupling, which is quite large in the IO radical ($A = -2091 \pm 40$ cm^{-1} = -25.0 ± 0.5 kJ/mol)[31,21] and must be considered in any quantitative calculations on this molecule. One method is to correct the nonrelativistic ab initio energy using the experimental *A* value, as done in ref 32. We chose instead to perform calculations on the closed-shell IO^- ($^1\Sigma^+$) anion and to accept the experimental value for the electron affinity EA(IO) = 229.4 ± 0.6 kJ/mol.[31,21] The congeneric metathesis reactions 6−9 were used to calculate the enthalpy of formation for the hypoiodite anion (IO^-). To assess the

$$IO^- + Cl^- \rightarrow ClO^- + I^- \tag{6}$$

$$IO^- + Cl_2 \rightarrow ClO^- + ICl \tag{7}$$

$$IO^- + Br^- \rightarrow BrO^- + I^- \tag{8}$$

$$IO^- + Br_2 \rightarrow BrO^- + IBr \tag{9}$$

reliability of the procedures, the same computations were performed for the analogous bromine species using reactions 10 and 11.

$$BrO^- + Cl^- \rightarrow ClO^- + Br^- \tag{10}$$

$$BrO^- + Cl_2 \rightarrow ClO^- + BrCl \tag{11}$$

For the thermochemistry of hypoiodous acid, HOI, we chose reactions 12−17. As a check, analogous calculations were done for HOBr exploiting the experimental data associated with reactions 18−20. Note that reactions 13 and 16 require our calculated thermochemical values for IO^- in addition to experimental reference data.

$$HOI + Cl^- \rightarrow I^- + HOCl \tag{12}$$

$$HOI + ClO^- \rightarrow IO^- + HOCl \tag{13}$$

$$HOI + Cl_2 \rightarrow ICl + HOCl \tag{14}$$

$$HOI + Br^- \rightarrow I^- + HOBr \tag{15}$$

$$HOI + BrO^- \rightarrow IO^- + HOBr \tag{16}$$

$$HOI + Br_2 \rightarrow IBr + HOBr \tag{17}$$

$$HOBr + Cl^- \rightarrow Br^- + HOCl \tag{18}$$

$$HOBr + ClO^- \rightarrow BrO^- + HOCl \tag{19}$$

$$HOBr + Cl_2 \rightarrow BrCl + HOCl \tag{20}$$

Weighted Averages and Estimation of Uncertainties. If a thermochemical study of a molecule includes the results of calculations using N_{basis} basis sets and N_{rx} reactions, then the number of computed reaction energies is $N = N_{basis}N_{rx}$. Since the reactions and basis sets vary in quality, simply averaging the N values is inappropriate. Uncertainties δ_i may be estimated for each value on the basis of the degree of correlation balance achieved, where we define the correlation balance to be the discrepancy in reaction energy derived from HF and CCSD(T) calculations. A rather arbitrary constant term is included to reflect what may be considered a significant difference in the correlation balance; we choose a value of 4 kJ/mol (eq 21).

$$\delta_i = s(|\Delta E_{CCSD(T)} - \Delta E_{HF}| + 4\ \text{kJ/mol}) \tag{21}$$

Thus, we consider differences in correlation balance of less than 4 kJ/mol to be insignificant. The final results are reasonably insensitive to the value of this parameter. We then compute a weighted average using the corresponding weights $w_i = \delta_i^{-2}/\sum\delta_j^{-2}$, so that $\sum w_i = 1$. The weights w_i are independent of the proportionality constant *s*, which is discussed further below. This weighting scheme emphasizes reactions that more effectively balance the correlation energy. If $x_i = \Delta E_{CCSD(T)}$ is the reaction energy calculated at the CCSD(T) level for the *i*th combination of basis set and reaction scheme, then the average value is computed in the usual way using eq 22.

$$\bar{x} = \sum_{i=1}^{N} w_i x_i \tag{22}$$

A value for the proportionality constant *s* is needed to estimate absolute uncertainties. Ideally, this would be obtained from the error distribution calculated for a statistically large number of molecules with well-established experimental enthalpies of formation. This was not feasible in the present study. Instead, we have chosen a value $s = 0.2$ for the reasons (1) it reproduces mean unsigned deviations from $\bar{x}$ fairly well, and (2) it corresponds approximately to the deficit in correlation effects usually observed for correlated calculations.[33]

As discussed in the Introduction, uncertainty estimates are very important in most applications of thermodynamics data. We suggest that these estimates be constructed by considering (1) the balance in the treatment of electron correlation, (2) the uncertainties in the experimental reference data, and (3) the scatter among the values obtained using different combinations of basis set and reaction scheme.

For the *i*th combination of basis set and reaction scheme, we represent the combined standard uncertainties in the experimental data by ϵ_i and define the combined experimental−theoretical value by $u_i = (\delta_i^2 + \epsilon_i^2)^{1/2}$. We then estimate the total combined uncertainty $\bar{u}$ using eq 23. In favorable cases the experimental uncertainties are negligible, but they become more important as the quality of the calculations approaches or exceeds the quality of the auxiliary experimental data. In some cases it is difficult to divine the precise meaning of reported experimental uncertainties. We have assumed in the present work that the reported uncertainties in the experimental data represent 2σ, so we divide them by 2 before use. We intend the values calculated using eq 23 to approximate the standard uncertainties (1σ).

$$(\bar{u})^2 = \sum w_i u_i^2 + \frac{\sum w_i (x_i - \bar{x})^2}{(N-1)} \tag{23}$$

This method for estimating standard uncertainties is intended as a pragmatic starting point and may require further refinement. In particular, (1) the proportionality constant *s* could be determined from an actual distribution, as described above, (2) we have not addressed the implications of dependencies among the component uncertainties, and (3) we have not investigated whether the quantities x_i properly describe potential sources of error that were not encountered in the present study (e.g., spin contamination, nondynamical correlation).

Auxiliary Thermochemistry. The supporting data are listed in Table 1. Most were taken from the 1989 compilation by Gurvich et al.,[34] sometimes in combination with electron affinities from ref 21.

For HOCl, recent work leads us to depart from the value $\Delta_f H^\circ_{298} = -75.7 \pm 5.0$ kJ/mol given in ref 34. The rate constant for the reaction $Cl + HOCl \rightarrow Cl_2 + OH$ has been measured very recently, and a value $\Delta_f H^\circ_{298}(\mathrm{HOCl}) = -75.1$ kJ/mol was derived.[35] We reanalyze these results, as described below, to derive a slightly different value and an uncertainty estimate. Averaging the results from Table 1 of ref 35 leads to $k_f = (2.26 \pm 0.25) \times 10^{-12}$ cm^3/s (1σ assumed). Combining this with the reverse rate[36] $k_r = (6.70 \pm 0.72) \times 10^{-14}$ cm^3/s (1σ) leads to $K_{eq} = 33.7 \pm 5.2$ (1σ) at 298 K and hence $\Delta_r G^\circ_{298} = -8.7 \pm 0.4$ kJ/mol (1σ). Entropy data from ref 34 lead to $\Delta_r S^\circ_{298} = 5.05$ J/(mol·K) and thus $\Delta_r H^\circ_{298} = -7.2 \pm 0.4$ kJ/mol (1σ). Using enthalpy data from ref 34, we finally obtain $\Delta_f H^\circ_{298}(\mathrm{HOCl}) = -74.8 \pm 1.2$ kJ/mol (2σ) and $\Delta_f H^\circ_0(\mathrm{HOCl}) = -71.8 \pm 1.2$ kJ/mol (2σ), which we adopt. This is consistent with the earlier values but more precise.

The revision in the thermochemistry for HOCl has implications for other molecules. For example, there have been three measurements (at $T = 333$, 295, and 298 K) of the equilibrium constant for the reaction $\mathrm{H_2O} + \mathrm{Cl_2O} = 2\mathrm{HOCl}$.[37−39] After being corrected to 298.15 K using data from ref 34, the three measurements[37−39] correspond to consistent reaction enthalpies $\Delta_r H^\circ_{298}$ of 10.6 ± 0.3, 11.5 ± 0.7, and 10.8 ± 0.6 kJ/mol (2σ), respectively. The new HOCl value can be used to deduce the corresponding values for the enthalpy of formation. Averaging leads to $\Delta_f H^\circ_{298}(\mathrm{Cl_2O}) = 81.3 \pm 1.8$ kJ/mol and $\Delta_f H^\circ_0(\mathrm{Cl_2O}) = 83.1 \pm 1.8$ kJ/mol (2σ), which we recommend. This agrees very well with the values in ref 40 and is consistent with the value in ref 34 but more precise. A somewhat lower but marginally consistent value of 77.2 ± 3.5 kJ/mol (298 K) was derived recently from photoionization appearance energy measurements.[41]

For HOBr, we again accept recent kinetics measurements to derive experimental thermochemistry more reliable than the much-cited lower limit $\Delta_f H^\circ_{298}(\mathrm{HOBr}) \geq -56.2 \pm 1.8$ kJ/mol.[42] Rate constants for the forward[43,44] and reverse[43,36] reactions of HOBr with chlorine atoms have been measured. We average[45] these values to obtain $K_{eq} = [(8.9 \pm 0.3) \times 10^{-11}]/[(1.49 \pm 0.62) \times 10^{-12}] = 59.7 \pm 25.0$ (uncertainties representing 2σ) for the reaction $\mathrm{HOBr} + \mathrm{Cl} \rightleftharpoons \mathrm{BrCl} + \mathrm{OH}$. This implies a free energy change of -10.1 ($+1.3/-0.9$) kJ/mol, which we simplify to $\Delta_r G^\circ_{298} = -9.9 \pm 1.1$ kJ/mol. Using auxiliary data from refs 34 and 46, we finally obtain $\Delta_f H^\circ_{298}(\mathrm{HOBr}) = -60.5 \pm 1.1$ kJ/mol and $\Delta_f H^\circ_0(\mathrm{HOBr}) = -50.0 \pm 1.1$ kJ/mol, which we adopt.

There has also been a recent experiment in which HOBr was photodissociated and the energy disposal fully characterized. The bond strength $D_0(\mathrm{HO{-}Br})$ was estimated to be 206.1 ± 4 kJ/mol.[47] Using data from ref 34, we then derive $\Delta_f H^\circ_0(\mathrm{HOBr}) = -49.1 \pm 4$ kJ/mol, in excellent agreement with the kinetics value and with a recent G2 calculation.[46]

The updated results for HOBr influence the thermochemical values for other molecules. In particular, we use the equilibrium constant[48] $K_{eq}(\mathrm{H_2O} + \mathrm{Br_2O} \rightleftharpoons 2\ \mathrm{HOBr}) = 0.02$ ($\pm$ 0.01 assumed), thermochemical data from refs 34 and 46, and thermochemical functions calculated from experimental data compiled in ref 49 to derive free energy, entropy, and enthalpy changes of 9.7 ± 1.2 kJ/mol, 16.4 J/(mol·K), and 14.6 ± 1.2 kJ/mol, respectively, and hence $\Delta_f H^\circ_{298}(\mathrm{Br_2O}) = 106.2 \pm 2.5$ kJ/mol. This agrees excellently with a very recent measurement (107.1 ± 3.5 kJ/mol) based upon photoionization appearance energies.[50] We also note that the thermochemistry for many other compounds may be derived using the interrelationships in ref 49.

Spectroscopy of IO$^+$. Since the adiabatic ionization energy of IO has been determined in a photoionization threshold measurement,[51] $\mathrm{IE(IO)} = 9.735 \pm 0.017$ eV, the thermochemistry of the ion IO$^+$ can be derived from that of neutral IO. To calculate the thermodynamic functions for this species at temperatures above 0 K, rotational and vibrational constants are needed. An equilibrium internuclear distance of 1.8245 Å was obtained for $\mathrm{IO^+}(^3\Sigma^-)$ at the frozen-core CCSD(T)/6-311+G(3df) level (4d electrons active). At the same level of theory, a series of single-point energy calculations was performed to construct a potential energy curve. Vibrational energy levels were computed using the variational Fourier grid Hamiltonian method.[52] The ZPVE was calculated to be 379.5 cm^{-1}, and the constants $\omega_e = 763.0$ cm^{-1}, $\omega_e x_e = 8.0$ cm^{-1}, and $\omega_e y_e = 0.3$ cm^{-1} were derived.

The spin splitting in IO$^+$ has not been reported. However, the photoionization spectrum of IO is expected to contain this information and has been reported.[51] The two major features at low ionization energy were assigned to $\mathrm{IO^+}$ (X $^3\Sigma^-$ $v' = 0,1$) $\leftarrow$ IO (X $^2\Pi_{3/2}$ $v'' = 0$). Their spacing, 1060 ± 160 cm^{-1}, was thus assigned to the vibrational fundamental in the ground electronic state of IO$^+$.[51] This is 40% higher than the value from our high-level ab initio calculations and is therefore suspect. In support of our calculated vibrational frequency, we note that removing a π^* electron from IO$^-$ increases ω_e by about 100 cm^{-1}, to 682 cm^{-1}.[21] Removing another π^* electron would be expected to raise the frequency another 100 cm^{-1} to about 780 cm^{-1}. Our value of 763 cm^{-1} is therefore quite reasonable.

Ab initio Franck−Condon factors favor the 0−0 ionization of IO over the 1−0 by a factor of 2.0.[53] The ratio in the IO photoionization spectrum is instead ~0.4, which is additional evidence against assigning the interval as a vibrational quantum. Instead, we reassign the two steps to represent transitions to the two sublevels of the ground state of the ion, $\mathrm{IO^+}$ (X $^3\Sigma^-_{\pm1,0}$ $v' = 0$) $\leftarrow$ IO (X $^2\Pi_{3/2}$ $v'' = 0$), so that $\lambda_0(\mathrm{IO^+}) = 530 \pm 80$ cm^{-1}. The expected statistical intensity ratio is then 0.5, in acceptable agreement with the observed ratio of about 0.4. This spectral reassignment is also supported by a relativistic, multireference CI calculation that predicts a spin splitting of about 900 cm^{-1}.[53]

Results and Analysis

BrO$^-$. The experimental electron affinity $\mathrm{EA(BrO)} = 227.0 \pm 0.6$ kJ/mol[21] and the enthalpy of formation $\Delta_f H^\circ_0(\mathrm{BrO}) = 133.4 \pm 2.4$ kJ/mol[34] imply $\Delta_f H^\circ_0(\mathrm{BrO^-}) = -93.6 \pm 2.5$ kJ/mol. We accept this value as an experimental benchmark.

The values for $\Delta_f H^\circ_0(\mathrm{BrO^-})$ obtained from reactions 10 and 11 using the various approximations are shown in Table 2. Examining Table 2 leads to several observations. (1) Both reactions are fairly successful in canceling systematic errors since the results from MP2, CCSD, and CCSD(T) calculations differ by ≤ 4.2 kJ/mol. (2) Correlation errors cancel more completely for reaction 11 than for reaction 10 since the HF and correlated results agree better (7 kJ/mol for reaction 11 vs 20 kJ/mol for reaction 10). (3) The discrepancy between the CCSD(T) results from the two reactions is 5.8, 2.8, 2.1, and 4.8 kJ/mol for the PBS, 6-311+G(3df), 6-311+2G(3df), and ECP basis sets, respectively. (4) The values from reactions 10 and 11 are lower than the experimental value, and the full CCSD(T) results from reaction 11 are generally closer to the experimental value than are those from reaction 10. (5) The frozen-core approximation is excellent for the 6-311+G(3df), 6-311+2G(3df), and PBS basis sets and is good for the ECP. (6) Within the full CCSD(T) method, the PBS results agree least well with experiment and with the results obtained using the other basis sets.

Our most thorough and presumably most reliable calculations are those employing the CCSD(T) approximation and with no orbitals frozen. The corresponding results are indicated by bold

TABLE 2: *Ab Initio* Enthalpy of Formation (kJ/mol) of BrO^- ($^1\Sigma^+$) at 0 K Derived from Reactions 10 and 11 Using Various Levels of Calculation, Basis Sets, and Active Spaces. The Experimental Value Is −93.6 ± 2.5 kJ/mol (See Text)

	reaction 10				reaction 11			
basis set	CCSD(T)	CCSD	MP2	HF	CCSD(T)	CCSD	MP2	HF
PBS								
valence active	−106.9	−105.5	−104.4	−87.7	−101.7	−100.7	−99.6	−95.4
3d and valence active	−108.1	−105.8	−104.6		−101.3	−100.0	−99.6	
all electrons active	**−108.0**	−105.5	−104.6		**−102.2**	−100.8	−100.3	
6-311+G(3df)								
valence active	−99.8	−98.6	−101.0	−86.5	−95.9	−94.8	−94.2	−91.1
3d and valence active	−99.8	−98.2	−100.6		−96.0	−95.0	−95.5	
all electrons active	**−98.8**	−97.2	−99.8		**−96.0**	−94.9	−95.4	
6-311+2G(3df)								
valence active	−97.5	−95.9	−97.9	−84.9	−98.4	−97.2	−96.4	−92.5
3d and valence active	−97.7	−95.6	−97.8		−98.5	−97.4	−97.6	
all electrons active	**−96.6**	−94.6	−96.9		**−98.7**	−97.6	−97.7	
ECP								
valence active	−104.6	−103.0	−105.5	−90.4	−99.7	−99.7	−100.1	−100.1
all electrons active	**−101.2**	−99.8	−102.3		**−96.4**	−100.6	−99.5	

TABLE 3: *Ab Initio* Enthalpy of Formation (kJ/mol) of IO^- ($^1\Sigma^+$) at 0 K Derived from Reactions 6 and 7 Using Various Levels of Calculation, Basis Sets, and Active Electrons

	reaction 6				reaction 7			
basis set	CCSD(T)	CCSD	MP2	HF	CCSD(T)	CCSD	MP2	HF
PBS								
valence active	−122.0	−119.4	−128.7	−86.8	−116.7	−115.0	−123.1	−100.9
4d and valence active	−127.1	−122.9	−129.5		−116.3	−114.2	−122.1	
all electrons active	**−129.3**	−124.8	−132.2		**−117.0**	−114.7	−122.6	
6−311+G(3df)								
valence active	−112.7	−110.3	−122.4	−86.5	−111.0	−108.8	−116.7	−97.3
4d and valence active	−113.7	−110.7	−122.5		−112.2	−110.0	−118.9	
all electrons active	**−112.0**	−109.1	−120.9		**−112.4**	−110.1	−119.0	
6−311+2G(3df)								
valence active	−108.4	−105.5	−117.1	−83.3	−114.3	−111.8	−119.3	−99.0
4d and valence active	−110.5	−107.0	−118.5		−115.8	−113.3	−122.0	
all electrons active	**−108.7**	−105.0	−116.7		**−116.3**	−113.7	−122.4	
ECP								
valence active	−117.5	−114.5	−125.2	−91.1	−111.8	−109.6	−117.5	−98.8
all electrons active	**−114.1**	−111.3	−122.1		**−111.9**	−109.7	−117.8	

TABLE 4: *Ab Initio* Enthalpy of Formation (kJ/mol) of HOBr at 0 K Derived from Reactions 18−20 Using Various Levels of Calculation, Basis Sets, and Active Electrons. The Experimental Value is −50.0 ± 1.1 kJ/mol (See Text)

	reaction 18				reaction 19				reaction 20			
basis set	CCSD(T)	CCSD	MP2	HF	CCSD(T)	CCSD	MP2	HF	CCSD(T)	CCSD	MP2	HF
6−311+G(3df,2p)												
valence active	−51.8	−50.9	−56.7	−37.7	−45.6	−45.8	−49.3	−44.7	−47.9	−47.0	−50.0	−42.2
3d and valence active	−52.0	−50.5	−55.0		−45.7	−45.9	−47.9		−48.2	−47.3	−49.8	
all electrons active	**−50.9**	−49.5	−54.3		**−45.7**	−45.9	−48.1		**−48.1**	−47.2	−49.9	
6−311+2+G(3df,2p)												
valence active	−48.5	−47.2	−52.9	−35.6	−44.6	−44.9	−48.6	−44.3	−49.4	−48.5	−51.4	−43.3
3d and valence active	−48.8	−47.0	−51.3		−44.7	−44.9	−47.1		−49.6	−48.8	−51.2	
all electrons active	**−47.6**	−45.8	−50.5		**−44.5**	−44.8	−47.2		**−49.6**	−48.7	−51.4	
ECP												
valence active	−55.4	−54.0	−58.6	−40.4	−44.3	−44.6	−46.7	−43.6	−51.6	−50.8	−53.2	−46.4
all electrons active	**−51.7**	−50.5	−55.2		**−44.1**	−44.4	−46.4		**−51.1**	−50.3	−52.9	

type in Tables 2−5. Employing the eight such results in Table 2 according to eqs 21−23 leads to the predicted value $\Delta_f H°_0(BrO^-) = -98.3 \pm 5.0$ kJ/mol (2σ), in agreement with the experimental value. If the results from the PBS basis are omitted, the remaining six values yield $\Delta_f H°_0(BrO^-) = -97.3 \pm 4.6$ kJ/mol (2σ), in slightly better agreement with the benchmark.

IO^-. The values for $\Delta_f H°_0(IO^-)$ obtained from reactions 6 and 7 using the various approximations are shown in Table 3. Comparing Tables 2 and 3 shows that the variations in $\Delta_f H°_0(IO^-)$ derived from reactions 6 and 7 and using different levels of theory and basis sets are fully analogous to those discussed for $\Delta_f H°_0(BrO^-)$. The results obtained using reactions 8 and 9 are similar but, for conciseness, are not tabulated. Employing the 16 full-CCSD(T) results (four basis sets × four reactions) leads to a value $\Delta_f H°_0(IO^-) = -109.7 \pm 8.5$ kJ/mol (2σ). However, among the CCSD(T) values for BrO^-, the PBS results disagree with those from the other two basis sets and are farthest from the accepted value (Table 2). Since the disagreement with the other basis sets persists for IO^- (Table 3), we expect the PBS results also to be the least accurate for IO^- and discard them. The remaining 12 results lead to a value $\Delta_f H°_0(IO^-) = -108.7 \pm 7.6$ kJ/mol (2σ). Using enthalpy differences from ref 34 and calculated anharmonically from the experimental data in Table 1, this implies $\Delta_f H_{298}(IO^-) = -110.5 \pm 7.6$ kJ/mol in the ion convention.[30]

IO. No calculations were done on this radical explicitly, but its thermochemistry is linked to that of IO^- by the experimental electron affinity EA(IO) = 2.378 ± 0.006 eV = 229.4 ± 0.6 kJ/mol.[31,21] This leads to $\Delta_f H°_0(IO) = 120.7 \pm 7.6$ kJ/mol (2σ).

TABLE 5: *Ab Initio* Enthalpy of Formation (kJ/mol) of HOI at 0 K Derived from Reactions 12−14 Using Various Levels of Calculation, Basis Sets, and Active Electrons

	reaction 12				reaction 13				reaction 14			
basis set	CCSD(T)	CCSD	MP2	HF	CCSD(T)	CCSD	MP2	HF	CCSD(T)	CCSD	MP2	HF
6−311+G(3df,2p)												
valence active	−55.9	−54.5	−63.1	−34.1	−51.7	−52.7	−49.2	−56.1	−54.2	−53.0	−57.4	−44.9
4d and valence active	−56.6	−54.5	−61.0		−51.4	−52.4	−47.0		−55.1	−53.9	−57.4	
all electrons active	**−54.7**	−52.7	−59.3		**−51.2**	−52.2	−46.9		**−55.0**	−53.8	−57.4	
6−311+2+G(3df,2p)												
valence active	−50.4	−48.9	−57.3	−32.1	−50.5	−51.9	−48.7	−57.3	−56.3	−55.2	−59.5	−47.8
4d and valence active	−52.4	−50.2	−56.6		−50.3	−51.7	−46.6		−57.6	−56.5	−60.1	
all electrons active	**−50.3**	−48.2	−54.6		**−50.0**	−51.5	−46.4		**−57.8**	−56.7	−60.3	
ECP												
valence active	−63.3	−61.2	−68.2	−40.1	−54.3	−55.2	−51.5	−57.5	−57.6	−56.3	−60.5	−47.8
all electrons active	**−59.6**	−57.7	−64.7		**−54.0**	−54.9	−51.2		**−57.4**	−56.1	−60.5	

Using enthalpy differences from ref 34 and calculated anharmonically from the experimental data in Table 1, we then obtain $\Delta_f H°_{298}(IO) = 118.8 \pm 7.6$ kJ/mol.

IO$^+$. No calculations were done on this ion explicitly, but its thermochemistry is linked to that of IO by the experimental ionization energy IE(IO) = 9.735 ± 0.017 eV = 939.3 ± 1.6 kJ/mol.[51] This leads to $\Delta_f H°_0(IO^+) = 1060.0 \pm 7.8$ kJ/mol. Assuming the sublevels of IO$^+$ (X $^3\Sigma^-_{\pm 1,0}$) to have the same spectroscopic constants (see above), we then obtain $\Delta_f H_{298}(IO^+) = 1058.1 \pm 7.8$ kJ/mol in the ion convention.[30]

HOBr. In this case we use the experimental benchmark derived above, $\Delta_f H°_0(HOBr) = -50.0 \pm 1.1$ kJ/mol. Since the PBS basis set appeared inadequate for the thermochemistry of BrO$^-$ and IO$^-$, we did not use it subsequently for HOBr or HOI. The values for $\Delta_f H°_0$(HOBr) obtained from reactions 18−20 using the various approximations are shown in Table 4. Some observations are that (1) the CCSD(T) and HF results differ by ≤1 kJ/mol for reaction 19 and (2) the results from reaction 20 agree best with the experimental value. Reaction 19 is the only isodesmic reaction of the three. The excellent balance of correlation energy is therefore expected on chemical grounds. Performing the weighted average of the nine full-CCSD(T) results in Table 4 using the methods recommended above, we obtain $\Delta_f H°_0(HOBr) = -45.9 \pm 4.1$ kJ/mol (2σ), in marginal agreement with the benchmark.

HOI. The results using three basis sets and reactions 12−14 are shown in Table 5. The results for reactions 15−17 are not shown, for conciseness. Averaging the corresponding 18 results yields $\Delta_f H°_0(HOI) = -55.2 \pm 6.9$ kJ/mol (2σ). Since reactions 13 and 16 depend upon our calculated value for $\Delta_f H°_0(IO^-)$, we also considered these reactions separately. Omitting the results of eqs 13 and 16 leads to $\Delta_f H°_0(HOI) = -55.6 \pm 4.7$ kJ/mol (2σ), and using only eqs 13 and 16 yields $\Delta_f H°_0(HOI) = -54.7 \pm 9.4$ kJ/mol (2σ). The good agreement among these three values indicates that our results for IO$^-$ and HOI are consistent. We calculate the thermal functions for HOI using the rigid-rotor, anharmonic-oscillator model. The geometry and anharmonicity constant x_{11} are from Table 1, and the remaining anharmonicity parameters are estimated from their values in HOBr and HOCl to be $x_{12} = -25$, $x_{13} = 0$, $x_{22} = -7.7$, $x_{23} = -7.4$, and $x_{33} = -2$ cm^{-1}. These constants are combined with the vibrational fundamentals from Table 1 to derive harmonic frequencies $\omega_1 = 3803.9$, $\omega_2 = 1099.6$, and $\omega_3 = 582.7$ cm^{-1}. These constants are combined with elemental data from ref 34 to derive the thermodynamic data in Table 6, including $\Delta_f H°_{298}(HOI) = -59.9 \pm 6.9$ kJ/mol (2σ). Note that the anharmonicity corrections are small; at 298 K they are $\Delta S° = 0.10$ J/(mol·K) and $\Delta \int C_p \, dT = 0.022$ kJ/mol. The irregularity in the variation of thermal functions with temperature is due to phase changes in the reference state of I_2.

TABLE 6: Recommended Gas-Phase Thermodynamic Properties of HOI, Calculated in the Rigid-Rotor, Anharmonic-Oscillator Model. The Uncertainty in $\Delta_f H°$ and $\Delta_f G°$ is 6.9 kJ/mol and Is Intended to Represent 2σ

T (K)	$C_p°$ (J/(mol·K))	$S°$ (J/(mol·K))	$H°_T - H°_0$ (kJ/mol)	$\Delta_f H°$ (kJ/mol)	$\Delta_f G°$ (kJ/mol)
0	0	0	0	−55.2	−55.2
50	33.26	193.2	1.66	−55.1	−58.0
100	33.40	216.3	3.33	−56.3	−61.2
150	34.32	230.0	5.02	−57.3	−63.5
200	35.84	240.1	6.77	−58.2	−65.4
250	37.53	248.2	8.60	−59.1	−67.1
298.15	39.11	255.0	10.45	−59.9	−68.6
300	39.17	255.2	10.52	−60.0	−68.6
350	40.66	261.4	12.52	−60.8	−70.0
400	41.97	266.9	14.58	−69.7	−71.0
500	44.05	276.5	18.89	−92.4	−69.1
600	45.60	284.7	23.38	−92.9	−64.4
700	46.83	291.8	28.00	−93.2	−59.6
800	47.86	298.1	32.74	−93.5	−54.8
900	48.78	303.8	37.57	−93.8	−49.9
1000	49.62	309.0	42.49	−94.0	−45.0

Discussion

BrO$^-$. Our most thorough and presumably most reliable calculations are those employing the CCSD(T) approximation and with no orbitals frozen. We thus have six values for $\Delta_f H°_0(BrO^-)$ corresponding to three reliable basis sets and two congeneric reactions. The averaged BrO$^-$ value of −97.3 ± 4.6 (2σ) is in error by −3.7 ± 5.2 kJ/mol relative to the accepted experimental value of −93.6 ± 2.5 kJ/mol. Such good agreement suggests that the overall approach is sound. We infer in particular that (1) the chemical match between chlorine and bromine is good and (2) using anionic schemes causes no problems. The second point is important because the weakest part of our approach here was expected to be its reliance on anions, which require large, diffuse basis sets. The basis sets employed appear to be sufficiently diffuse, including up to (2s2p1d, 1s1p) diffuse functions on heavy atoms and hydrogen, respectively. Indeed, the second set of diffuse functions appears unnecessary; the 6-311+G(3df,2p) basis is adequate.

IO$^-$, IO and IO$^+$. As for BrO$^-$, our most trustworthy calculations for IO$^-$ are those employing the CCSD(T) approximation and with no orbitals frozen. In this case we have 12 values for $\Delta_f H°_0(IO^-)$ corresponding to three reliable basis sets and four congeneric reactions. Judging from the result for BrO$^-$, we expect the averaged value $\Delta_f H°_0(IO^-) = -108.7 \pm 7.6$ kJ/mol (2σ) to be reliable. Although there are stronger relativistic effects for the heavier halogen, the associated errors are expected to be systematic and to cancel when using balanced-reaction energetics. Our value is substantially lower than the prediction $\Delta_f H°_0(IO^-) = -91.8$ kJ/mol from G2(ECP) calculations.[54] However, those results appear to contain an arithmetic error. Using G2(ECP) energies (which include

TABLE 7: Recommended Values of Enthalpies of Formation (Ion Convention, kJ/mol), Bond Energies (kJ/mol), and Standard Entropies (J/(mol·K))[a]

	$\Delta_f H°_0$	$\Delta_f H_{298}$	$D°_0$	D_{298}	$S°_{298}$
IO^-	-108.7 ± 7.6	-110.5 ± 7.6	167.1 ± 7.6	170.8 ± 7.6	235.0 ± 0.2
IO	120.7 ± 7.6	118.8 ± 7.6	233.3 ± 7.6	237.1 ± 7.6	239.6 ± 0.1
IO^+	1060.0 ± 7.8	1058.1 ± 7.8	302.4 ± 7.8	306.3 ± 7.8	233.4 ± 0.3
HOI	-55.2 ± 6.9	-59.9 ± 6.9	391.9 ± 10.3	396.7 ± 10.3	255.0 ± 0.1
			201.5 ± 6.9	206.0 ± 6.9	
HOBr	-50.0 ± 1.1	-60.5 ± 1.1	399.4 ± 2.6	404.3 ± 2.6	248[b]
			207.0 ± 1.1	211.7 ± 1.1	
HOCl	-71.8 ± 1.2	-74.8 ± 1.2	388.9 ± 1.2	394.4 ± 1.2	236.6[c]
			230.5 ± 1.2	235.5 ± 1.2	

[a] For IO^+ and IO^-, bond strengths are relative to $I^+ + O$ and to $I^- + O$, respectively. For HOX, the larger bond strength is for $D(H-OX)$ and the smaller for $D(HO-X)$. Entropies are calculated in the rigid-rotor, anharmonic-oscillator model. Uncertainties are intended to represent 2σ. [b] Reference 46. [c] Reference 34.

ZPVE) from refs 54 and 4 leads to $E(I^-) + E(O) - E(IO^-) = -11.460\,56 - 74.982\,03 + 86.503\,68 = 0.061\,09$ hartree $= 160.4$ kJ/mol, which in turn implies $\Delta_f H°_0(IO^-) = \Delta_f H°_0(I^-) + \Delta_f H°_0(O) - 160.4$ kJ/mol $= -188.0 + 246.8 - 160.4 = -101.6$ kJ/mol. Another source of error in the G2(ECP) calculations was the use of an MP2 bond length for IO^- which is 0.066 Å greater than the experimental value.[21] Using experimental values for r_e, ω_e, and μ and the simple harmonic model $E(r) = {}^1\!/_2 k(r - r_e)^2 = 2\pi^2\omega_e^2\mu(r - r_e)^2$, we expect the resulting energy for IO^- to be too high by 3.7 kJ/mol. This leads to a total discrepancy of $(-101.6 - 3.7) - (-108.7) = 3.4$ kJ/mol between the G2(ECP) result and ours. Since our calculations involved larger basis sets and balanced reaction schemes, we favor our lower value $\Delta_f H°_0(IO^-) = -108.7 \pm 7.6$ kJ/mol.

The energetics for IO, derived from our results for IO^- by applying the experimental electron affinity,[21,31] are $\Delta_f H°_0(IO) = 120.7 \pm 7.6$ and $\Delta_f H°_{298}(IO) = 118.8 \pm 7.6$ kJ/mol (2σ). These values correspond[34] to bond strengths $D_0(I-O) = 233 \pm 8$ and $D_{298}(I-O) = 237 \pm 8$ kJ/mol.

We can compare our results for $\Delta_f H°_0(IO)$ and $D_0(I-O)$ with values in the literature. There have been several attempts to determine the bond energy of IO by vibrational extrapolation, but the results are quite sensitive to the choice of extrapolating function and the vibrational levels used.[55-59] A measurement of the dissociative equilibrium $IO \rightleftharpoons I + O$ in flames yields a bond strength of 256 ± 25 kJ/mol after updating the appropriate auxiliary data.[60] Two independent studies of the energy disposal in the reaction $O + ICl \rightarrow IO + Cl$ derived bond energies of 222 ± 13 and 230 ± 8 kJ/mol.[61,62] Kinetics experiments have placed an upper limit on $\Delta_f H°_{298}(IO)$ of about 119 kJ/mol[63] and more recently $\Delta_f H°_{298}(IO) \lesssim 120.5$ kJ/mol.[64] Bracketing results from the most recent published kinetics[65] suggest that 108 kJ/mol $\leq \Delta_f H°_{298}(IO) \leq 115$ kJ/mol, which corresponds to 248 kJ/mol $\geq D_{298}(I-O) \geq 241$ kJ/mol. If borne out by direct measurements, this indicates that IO is slightly more stable than our prediction $\Delta_f H°_{298}(IO) = 118.8 \pm 7.6$ kJ/mol but probably within our uncertainty range.

There has also been an estimate $\Delta_f H°_{298}(IO) = 127.8 \pm 4.2$ kJ/mol, or $D_0(I-O) = 224.3 \pm 4.2$ kJ/mol, based upon careful G2 and G2(QCI) studies of two congeneric reactions involving ClO and BrO.[32] If the kinetics bracketing results are reliable, the G2(QCI) result is in error by $\geq 12.8 \pm 4.2$ kJ/mol. The discrepancy is probably due to an accumulation of small errors such as in bond length, in the treatment of open-shell systems, and in the differential correlation energy. We favor our calculated value, $\Delta_f H°_{298}(IO) = 118.8 \pm 7.6$ kJ/mol, since it is consistent with the kinetics experiments.

For IO^+, we apply the experimental ionization energy[51] to our energetics for neutral IO to obtain $\Delta_f H°_0(IO^+) = 1060.0 \pm 7.8$ kJ/mol (2σ). The only previously reported enthalpy of formation is $\Delta_f H°_0(IO^+) \approx 1067$ kJ/mol, based upon an estimate $\Delta_f H°_0(IO) \approx 128$ kJ/mol and the measured ionization energy.[51] We combine the same ionization energy with the more reliable neutral thermochemistry from the present work.

HOBr and HOI. For HOBr our predicted enthalpy of formation is in error by $+4.1 \pm 4.2$ kJ/mol relative to the experimental benchmark, just within the uncertainty limits. We therefore expect our value for HOI, $\Delta_f H°_0(HOI) = -55.2 \pm 6.9$ kJ/mol, to be reliable but perhaps a bit high. Prior values are (1) an estimate[42] $\Delta_f H°_0(HOI) \approx -36$ kJ/mol, (2) an estimate $\Delta_f H°_0(HOI) = -42.7 \pm 2.5$ kJ/mol,[51] and (3) a G2(ECP) result of -44.7 kJ/mol, based upon the calculated atomization energy.[54] Both estimates were based upon the trend in the bond energy ratios $r(X) \equiv D_0(HO-X)/D_0(X-O)$.[42] Using the current values for chlorine and bromine from ref 34 and Table 1 yields $r(Cl) = (240.5 \pm 1.2)/(265.4 \pm 0.1) = 0.906 \pm 0.005$ and $r(Br) = (207.0 \pm 1.1)/(231.3 \pm 2.4) = 0.895 \pm 0.010$. Our values for IO and HOI yield $r(I) = (201.5 \pm 6.9)/(233.3 \pm 7.6) = 0.864 \pm 0.041$, in satisfactory agreement with a linear extrapolation (0.884) from the ratios for Cl and Br. The G2(ECP) result for $\Delta_f H°_0(HOI)$ was based upon calculated atomization energies.[54] As discussed in the Introduction, atomization reactions are especially poor for thermochemical calculations. Errors in geometry and vibrational frequencies can also be problematic, as pointed out above for IO^-.

Bond strengths are summarized in Table 7. The formation enthalpies for HOCl and HOBr recommended above, when combined with auxiliary data from ref 34, imply $D_0(H-OCl) = 388.9 \pm 1.2$ kJ/mol and $D_0(H-OBr) = 399.4 \pm 2.6$ kJ/mol. For HOI, our results imply $D_0(H-OI) = 392 \pm 10$ kJ/mol, similar to the congeneric values. The bond strengths $D_0(HO-X)$ corresponding to the revised experimental enthalpies of formation are $D_0(HO-Cl) = 230.5 \pm 1.2$ kJ/mol and $D_0(HO-Br) = 207.0 \pm 1.1$ kJ/mol. Our calculated thermochemistry implies a similar value for HOI, $D_0(HO-I) = 201 \pm 7$ kJ/mol. We omit fluorine from discussion because it often does not follow the trends of the heavier halogens.[8]

Conclusions

We have suggested the use of eqs 21 and 22 for averaging thermochemical results from ab initio calculations. We also suggest that eq 23 be used to estimate the standard uncertainties associated with such averaged results. These simple equations represent the first systematic attempt to estimate the uncertainties associated with ab initio energetics. Analogous procedures could probably be developed to aid in the prediction of other physical quantities by ab initio methods.

Using these new methods, test calculations on BrO^- and HOBr are in agreement with experimental benchmarks. Similar calculations yield enthalpies of formation for IO^-, IO, IO^+, and

HOI (Tables 6 and 7). Auxiliary to our calculations, we derive new and more precise enthalpies of formation for HOCl, Cl_2O, HOBr, and Br_2O on the basis of only published experimental results.

We find that typical diffuse basis sets are adequate and that a second set of diffuse functions is not necessary for negative ions such as BrO^- and IO^-. Basis sets developed for the calculation of electrostatic properties[25-28] give poorer thermochemical results than the more popular Pople-style basis sets. Results obtained using effective core potentials[29] are consistent with all-electron results but may be more sensitive to orbital freezing in correlated calculations.

Essentially all "ab initio" thermochemistry actually relies upon experimental thermochemistry. Experimental measurements are generally more reliable than calculations not only for thermochemical data but also for molecular geometries, vibrational constants, and electronic excitation energies. To achieve the best results, we find it advantageous to exploit experimental data as much as possible.

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