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# Computational Study of Enthalpies of Formation of OXO (X = Cl, Br, and I) and Their Anions

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The enthalpies of formation of OXO (X = Cl, Br, and I) and their anions were calculated using the Hartree−Fock, the second-order Møller−Plesset perturbation theory, the density functional theory with the B3LYP hybrid functional, and the coupled cluster theory using single and double excitation with a perturbational treatment of triplet excitation methods with two basis sets of triple-$\zeta$ plus polarization quality by employing several isodesmic (or congeneric) reactions. The weighted averages and their associated uncertainties for the enthalpies of formation were derived for these molecules using Irikura's procedure. The calculated standard enthalpies of formation at 0 K are 102.2 ± 6.5, 163.9 ± 7.1, 113.9 ± 10.3, −104.8 ± 6.5, −76.0 ± 7.0, and −135.0 ± 10.3 kJ/mol for OClO, OBrO, OIO, $OClO^-$, $OBrO^-$, and $OIO^-$, respectively. The derived values are in excellent agreement with the available experimental values.

## 1. Introduction

It is well-known that fluorine, chlorine, and bromine atoms are involved in the ozone depletion cycle. Recently, it has been demonstrated that some organic iodine compounds such as $CH_3I$ and $CH_2I_2$ are released into the atmosphere and that the photolysis of these iodocarbons leads to the production of iodine atoms, which react with other molecular species in the atmosphere to produce inorganic iodine compounds such as OI, HOI, and $IO_2$.[1−6] Since these iodine compounds are known to be implicated in ozone destruction cycle in the troposphere and lower stratosphere and to involve the formation of aerosol in the marine boundary layer, experimental and theoretical studies have been conducted to explore the structure and reactivity of iodine species.[7−19] Despite the better understanding of iodine chemistry in the atmosphere, the experimental thermodynamic data are scarce for iodine compounds found in the atmosphere. The experimental enthalpy of formation is available only for OI among the iodine oxide molecules that are known to play an important role in the atmosphere. Although the enthalpy of formation for OIO is important in understanding the iodine chemistry in the atmosphere, especially in the formation of cloud in the marine boundary layer, the experimental value is not known. There have only been two studies in which the enthalpy of formation of OIO has been investigated. Bedjanian et al. derived an upper limit for the enthalpy of formation of OIO, $\Delta_f H^\circ_{298} < 135$ kJ/mol.[9] Misra and Marshall estimated $\Delta_f H^\circ_0(\mathrm{OIO})$ to be 80.4 kJ/mol using the approximate QCISD(T)/6-311+G(3d,f) (equivalent to Gaussian-2 theory) energies with a single congeneric reaction scheme.[18] Since the bond dissociation energy of IO is less than that of ClO by about 80 kJ/mol,[20,21] the atomization energy of OIO is expected to be smaller than that of OClO. Although the enthalpy of formation for the Cl atom is higher than that of the I atom by about 15 kJ/mol, OIO is expected to be less stable than OClO. Since the $\Delta_f H^\circ_0(\mathrm{OClO})$ is about 99 kJ/mol,[20,21] $\Delta_f H^\circ_0(\mathrm{OIO})$ is expected to be higher than $\Delta_f H^\circ_0(\mathrm{OClO})$; however, the calculated $\Delta_f H^\circ_0(\mathrm{OIO})$ value is not consistent with the above line of reasoning. Thus, further investigation is required.

The goal of the present study was to estimate the enthalpies of formation of OXO and $OXO^-$ (X = Cl, Br, and I) by means of higher level quantum mechanical calculations with isodesmic (or congeneric) reaction schemes.

## 2. Calculational Methods

**A. Electronic Structure Calculations.** All calculations were performed with the Gaussian 98 program suite.[22] All geometries were fully optimized at the levels of the Hartree−Fock theory (HF), the second-order Møller−Plesset perturbation theory (MP2), the density functional theory with Becke three-parameter exchange potential and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP), and the coupled cluster theory using single and double excitations with a perturbational treatment of triplet excitation (CCSD[T]). The single-point energy calculations were performed at the CCSD(T,Full) level at the geometries optimized with the CCSD(T) method to account for core-valence correlation effects.

All calculations were performed using two different basis sets of triple-$\zeta$ plus polarization quality or better. The first set is 6-311+G(3d,f) for all atoms. This basis set is denoted as AE because all electrons are treated explicitly in the calculations. The second set utilizes the seven valence electron relativistic effective core potentials developed by Christiansen and coworkers for Br and I atoms.[23] The associated basis functions for Br and I atoms developed by Lee were used.[24] The basis functions for Br and I atoms consist of the (7s7p3d2f) primitive Gaussian functions and contract to the (4s4p3d2f) set. For other atoms besides Br and I atoms, the 6-311+G(3d,f) basis set was employed. This basis set is denoted as ECP to indicate that only valence electrons for Br and I atoms are treated explicitly.

The total energy for each molecular species was corrected by the zero-point vibrational energy (ZPVE) as listed in Table 1. For diatomic molecules, ZPVE = $(\omega_e/2) - (\omega_e\chi_e/4)$. For polyatomic molecules, ZPVE = $^1/_2\sum_i\omega_i + {}^1/_4\sum_{i\le j}\chi_{ij}$. When experimental vibrational frequencies are not available, the harmonic vibrational frequencies calculated at the level of B3LYP/AE are used.

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**B. The Choice of Isodesmic (Congeneric) Reaction Schemes.** When the isodesmic reactions are chosen to estimate the enthalpies of formation of various molecular species, open electronic shell molecules may be involved. If open shell molecules are included in the isodesmic reactions designed for the derivation of enthalpies of formation, the major sources of the errors in the derived values can be the spin−orbit splitting of the ground state of open shell molecules and the spin-contamination effect in the total energy of the open shell molecules calculated using unrestricted methods. To avoid such errors in the current study, the following scheme is employed to derive the enthalpies of formation for OXO (X = Cl, Br, and I). First, the enthalpies of formation for the OXO (X = Cl, Br, and I) anions were obtained using isodesmic (or congeneric) reactions, the calculated enthalpy of reaction, and the experimental enthalpies of formation of other chemical species involved in the reactions. Then, the enthalpies of formation of the OXO radicals were obtained by adding the experimental adiabatic electron affinities of the OXO (X = Cl, Br, and I) radicals to the corresponding enthalpies of formation of the OXO (X = Cl, Br, and I) anions. The experimental adiabatic electron affinity (AEA) is available for the OClO and OIO radicals but not for the OBrO radical. The experimental adiabatic electron affinity of OBrO was estimated by correcting the calculated one with the average of deviations between the experimental and calculated AEA for OClO and OIO.

The following isodesmic (or congeneric) reactions were used to derive the enthalpy of formation of the OXO anions. The reactions 1−3, 4−9, and 10−15 were used for $OClO^-$, $OBrO^-$, and $OIO^-$, respectively.

$$OClO^- + Cl^- \rightarrow ClO^- + ClO^- \tag{1}$$

$$OClO^- + Br^- \rightarrow ClO^- + BrO^- \tag{2}$$

$$OClO^- + I^- \rightarrow ClO^- + IO^- \tag{3}$$

$$OBrO^- + Cl^- \rightarrow BrO^- + ClO^- \tag{4}$$

$$OBrO^- + Br^- \rightarrow BrO^- + BrO^- \tag{5}$$

$$OBrO^- + I^- \rightarrow BrO^- + IO^- \tag{6}$$

$$OBrO^- + Cl^- \rightarrow OClO^- + Br^- \tag{7}$$

$$OBrO^- + OCl^- \rightarrow OClO^- + OBr^- \tag{8}$$

$$OBrO^- + BrCl \rightarrow OClO^- + Br_2 \tag{9}$$

$$OIO^- + Cl^- \rightarrow IO^- + ClO^- \tag{10}$$

$$OIO^- + Br^- \rightarrow IO^- + BrO^- \tag{11}$$

$$OIO^- + I^- \rightarrow IO^- + IO^- \tag{12}$$

$$OIO^- + Cl^- \rightarrow OClO^- + I^- \tag{13}$$

$$OIO^- + OCl^- \rightarrow OClO^- + OI^- \tag{14}$$

$$OIO^- + ICl \rightarrow OClO^- + I_2 \tag{15}$$

**C. Uncertainties in the Calculated Values.** When the above reactions are used to derive the enthalpy of formation for each molecule, the uncertainties in their calculated enthalpies of formation are expected to depend on the reaction scheme, calculation method, and basis set employed to derive the enthalpy of formation. Thus, they are different from each other. If there is a scheme for the estimation of the uncertainties in the calculated enthalpies, it is possible to derive statistically the weighted averages of enthalpy of formation and their associated uncertainties. It is very important to estimate the uncertainties associated with any specific derived value. Hassanzadeh and Irikura devised a procedure for the calculation of weighted average and its associated uncertainties for this purposes.[25] In the current study, their procedure was employed using ab initio energetics to predict molecular enthalpies of formation and to estimate their associated uncertainties.[25]

The procedure is explained well in the original work but is not well-known. Thus a brief description is given here to show how the weighted average and its uncertainty are computed in the present work. If the results of calculations using $N_{\mathrm{basis}}$ basis sets and $N_{\mathrm{rx}}$ reactions are employed for a thermochemical study of a molecule, then the number of computed reaction energies is $N = N_{\mathrm{basis}}N_{\mathrm{rx}}$. Hassanzadeh and Irikura thought that the uncertainty in the computed reaction energy using the *i*th combination of the basis set and reaction scheme, $\delta_i$, can be estimated based on the degree of electron correlation balance achieved and that the correlation balance is inversely proportional to the discrepancy in the reaction energies derived from HF and a calculation method employed at the post-Hartree−Fock level such as MP2, B3LYP, or CCSD(T). They expressed the uncertainty as in eq 16

$$\delta_i = 0.2(|\Delta E_{\mathrm{M}} - \Delta E_{\mathrm{HF}}| + 4\ \mathrm{kJ/mol}) \tag{16}$$

where M designates the calculation method. They defined the weight factor for the weighted average as the normalized reciprocal number of the squared uncertainty of the computed reaction energy, $\omega_i = \delta_i^{-2}/\sum_{j=1}^{N}\delta_j^{-2}$ so that $\sum\omega_i = 1$. If $x_i$ is the reaction energy for the *i*th combination of basis set and reaction scheme, the weighted average and its associated uncertainty can be computed using eqs 17 and 18, respectively.

$$\bar{x} = \sum_{i=1}^{N}\omega_i x_i \tag{17}$$

$$u_{\mathrm{x}} = \sqrt{\sum w_i \delta_i^{\,2} + \frac{\sum w_i (x_i - \bar{x})^2}{(N-1)}} \tag{18}$$

The last term under the square root in eq 18 is included to reflect the scatter among the values obtained using different combinations of the basis and reaction scheme.

These *N* reaction energies are used to derive *N* enthalpies of formation for the molecule. The uncertainty of each enthalpy of formation has another source of error in addition to the uncertainty in the computed reaction energy, that is, the combined uncertainty in the experimental data used in the derivation of the enthalpy of formation. The combined uncertainty in the experimental data can be obtained by using $\epsilon_i = \sqrt{\sum_j \epsilon_{i,j}^{\,2}}$ where $\epsilon_{i,j}$ is the uncertainty in the *j*th experimental datum. The combined experimental−theoretical uncertainty in the *i*th enthalpy of formation is expressed by $u_i = \sqrt{\delta_i^{\,2} + \epsilon_i^{\,2}}$. If $y_i$ is the enthalpy of formation for the *i*th combination of the basis set and reaction scheme, the weighted average value is computed in the usual way using $\bar{y} = \sum_{i=1}^{N}\omega_i y_i$ and its associated uncertainty is estimated using eq 19,

$$u_y = \sqrt{\sum w_i u_i^{\,2} + \frac{\sum w_i (y_i - \bar{y})^2}{(N-1)}} \tag{19}$$

In some cases it is difficult to determine the exact meaning of reported experimental uncertainties. In such cases, as Hassanzadeh and Irikura have suggested, the reported experimental uncertainties are assumed to represent $2\sigma$ where $\sigma$ is the standard deviation. The reported uncertainty in the current study is $2u_y$

**TABLE 1: The Molecular Geometries Optimized at the CCSD(T)/6-311+G(3d,f) Level (Bond Lengths in Å and Bond Angles in deg), Harmonic Vibrational Frequencies ($cm^{-1}$), Anharmonicity Constants ($cm^{-1}$), Zero-Point Vibrational Energies ($cm^{-1}$), and Enthalpies of Formation (kJ/mol) Employed in the Present Calculations and the Ab Initio Total Energies (hartree) Calculated at the CCSD(T,Full)/6-311+G(3d,f) Level**

| | $r_e$, ∠ | $w_e$[a] | $w_ex_e$[a] | ZPVE | $\Delta_fH°_0$[b] | total energy |
|---|---|---|---|---|---|---|
| $Cl^-$ | | | | | −229.1(0.2) | −459.882 146 |
| $Br^-$ | | | | | −206.77(0.23) | −2 573.046 144 |
| $I^-$ | | | | | −188.44(0.06) | −6 917.678 982 |
| $Cl_2$ | 2.001 | 559.751 | 2.694 3 | 279.20 | 0.0(0.0) | −919.595 970 |
| $Br_2$ | 2.304 | 323.321 | 1.077 42 | 162.39 | 45.7(0.1) | −5 145.923 475 |
| BrCl | 2.154 | 443.1 | 1.8 | 221.1 | 22.23(0.16) | −3 032.760 597 |
| $I_2$ | 2.688 | 214.548 | 0.061 625 9 | 107.12 | 65.5(0.1) | −13 835.173 015 |
| ICl | 2.340 | 382.18 | 1.450 | 190.73 | 19.03(0.04) | −7 377.400 653 |
| IBr | 2.486 | 267.38 | 0.774 | 133.50 | 49.75(0.14) | −9 490.561 550 |
| $ClO^-$ | 1.694 | 665 | 3.36 | 332 | −118.7(0.2) | −534.923 553 |
| $BrO^-$ | 1.823 | 575 | 4.74 | 286 | −93.6(2.5) | −2 648.087 943 |
| $IO^-$ | 1.955 | 581 | 4.37 | 289 | −109.0(2.7)[c] | −6 992.733 091 |
| $OClO^-$ | 1.574<br>113.6 | 823, 790<br>418 | | 1002 | −106.3(2.4)[c] | −610.003 246 |
| $OBrO^-$ | 1.725<br>112.1 | 718, 706<br>282 | | 854 | −66.7(4.5)[d] | −2 723.165 933 |
| $OIO^-$ | 1.875<br>109.0 | 711, 665<br>244 | | 810 | | −7 067.829 451 |

[a] Experimental spectroscopic constants for XY, $OX^-$ (X = Cl, Br, and I), and $OClO^-$ are from refs 20, 16, and 26, respectively. The harmonic vibrational frequencies for $OXO^-$ are taken from the B3LYP/AE calculations. [b] The enthalpies of formation are from ref 21 unless otherwise noted. [c] Reevaluated; see text. [d] This value is calculated using the experimental enthalpy of formation[27] and the adiabatic electron affinity estimated in the present work. See text.

and is placed in parentheses that are located just after the associated value.

**D. Auxiliary Thermochemical Data.** When an isodesmic reaction is employed to derive the enthalpy of formation for one specific chemical species, the experimental thermodynamic data of other species involved in the reaction are required. Table 1 presents the molecular geometries optimized at the CCSD(T)/6-311+G(3d,f) level, harmonic vibrational frequencies, anharmonicity constants, vibrational zero-point energies and enthalpies of formation, and the ab initio total energies for the species involved in the reactions 1−15. The spectroscopic constants for $Cl_2$, $Br_2$, $I_2$, ClBr, ClI, and BrI and for $ClO^-$, $BrO^-$, and $IO^-$ are taken from refs 20 and 16, respectively. The experimental vibrational frequencies for $OClO^-$ are taken from ref 26. The enthalpies of formation except for $OClO^-$, $OBrO^-$, and $OI^-$ are taken from ref 21. The enthalpies of formation for $OClO^-$ and $OI^-$ are reevaluated here (see below). The enthalpy of formation of $OBrO^-$ is derived from the enthalpy of formation and the estimated AEA of OBrO.[16,27]

Some experimental enthalpies of formation for some chemical species show large deviation from each other and have large uncertainties. In such cases, it is necessary to revise these experimental enthalpies of formation. The enthalpy of formation for OClO and IO are revised as follows.

*OClO.* The two experimental enthalpies of formation of OClO reported ($\Delta_fH^\circ_0$(OClO) = 107.5(10.0) kJ/mol and $\Delta_fH^\circ_0$(OClO) = 99.0(8.0) kJ/mol) show some difference and have large uncertainties.[20,21]

The recommended forward and reverse rate constants of the reaction Cl + OClO ⇆ 2ClO are $k_{f,298} = 5.80 \times 10^{-11}$ $cm^3$/(molecule·s) and $k_{r,298} = 3.50 \times 10^{-15}$ $cm^3$/(molecule·s), respectively.[28−31] The equations $K_{eq} = k_{f,298}/k_{r,298}$ and $\Delta G = -RT \ln K_{eq}$ lead to $\Delta_rG^\circ_{298} = -24.1(1.7)$ kJ/mol. Entropy data from Gurvich's compilation[21] give $\Delta_rS^\circ_{298} = 28.1(0.3)$ J/(K·mol). Then $\Delta_rH^\circ_{298} = -15.7(1.7)$ kJ/mol is obtained from the $\Delta G = \Delta H - T\Delta S$ relation. Using the enthalpy data from Gurvich's compilation, one obtains $\Delta_fH^\circ_0$(OClO) = 100.1(1.7) kJ/mol.

The recommended forward and reverse rate constants of the reaction Br + OClO ⇆ ClO + BrO can be expressed as $k_{f,298} = 3.40 \times 10^{-13}$ $cm^3$/(molecule·s) and $k_{r,298} = 6.80 \times 10^{-12}$ $cm^3$/(molecule·s), respectively.[31−33] Following the same procedure employed for the Cl + OClO ⇆ 2ClO case, one obtains $\Delta_fH^\circ_0$(OClO) = 102.9(3.3) kJ/mol. These two values for $\Delta_fH^\circ_0$(OClO) are consistent with each other. The weighted average of these two values and its uncertainty are computed using eqs 17 and 18. The weighted average, $\Delta_fH^\circ_0$(OClO) = 100.7(2.4) kJ/mol, which we adopt, is very similar to one of the available data, $\Delta_fH^\circ_0$(OClO) = 99.0(8.0) kJ/mol, but with much less uncertainty.

*IO.* There are several experimental enthalpies of formation for the IO molecule.[7,8,34] They range from 112.1 to 128.0 kJ/mol. Bedjanian et al. determined the forward and reverse rate constants, $k_{f,298} = 7.3 \times 10^{-12}$ $cm^3$/(molecule·s) and $k_{r,298} = 1.90 \times 10^{-13}$ $cm^3$/(molecule·s), for the I + OClO ⇆ ClO + IO reaction to determine the $\Delta_fH^\circ_0$(OClO).[9] Since the new $\Delta_fH^\circ_0$(OClO) value seems to be quite reliable, we use the rate constant data for the above reaction to determine the $\Delta_fH^\circ_0$(IO). With use of $\ln K_{eq} = 3.45$, the entropy and the enthalpy data from Gurvich's compilation lead to $\Delta_fH^\circ_0$(IO) = 120.4(2.6) kJ/mol, which we adopt. This value is consistent with the value of $\Delta_fH^\circ_0$(IO) = 120.7(7.6) kJ/mol derived computationally by Hassanzadeh and Irikura.[25]

## 3. Results and Discussion

**A. Estimation of Experimental Adiabatic Electron Affinity of OBrO.** The adiabatic electron affinities (AEAs) of OXO (X = Cl, Br, and I) have been calculated using the total energies calculated at the CCSD(T,Full) level. Zero-point vibrational energies are corrected using the experimental spectroscopic constants for the OXO neutral molecules and the OClO anion.[15,26,35−40] Since there are no experimental data for the OXO (X = Br and I) anions, the harmonic vibrational frequencies calculated at the B3LYP/AE level are employed. The calculated AEA values are listed in Table 2, along with the corresponding experimental values.[16,41]

The AEAs calculated with the CCSD(T,Full)/AE for OClO, OBrO, and OIO molecules are 195.9, 229.5, and 240.3 kJ/mol, respectively. The AEAs calculated with the CCSD(T,Full)/ECP

**TABLE 2: The Calculated and Experimental Adiabatic Electron Affinities (kJ/mol) of the OXO (X = Cl, Br, and I) Radicals**

| | OClO | OBrO | OIO |
|---|---|---|---|
| CCSD(T,Full)/AE | 195.9 | 229.5 | 240.3 |
| CCSD(T,Full)/ECP | | 229.3 | 236.1 |
| expt | 207.0(0.2)[a] | 240.1(1.3)[b] | 248.6(0.8)[c] |

[a] From ref 41. [b] The estimated value in this work. [c] From ref 16.

for OBrO and OIO molecules are 229.3 and 236.1 kJ/mol, respectively. The very small difference between two AEAs of OBrO in which the relativistic effect is expected to be negligible implies that the ECP calculation emulates the AE calculation very nicely. The small difference in two AEAs for OIO seems to originate from the inclusion of relativistic effect in the ECP calculation. Although the AEA of OIO calculated with the CCSD(T,Full)/ECP method includes these effects, it cannot include some portion of the electron correlation recovered in the CCSD(T,Full)/AE method due to the use of the effective core potentials. Thus, the arithmetic average of these two values is employed in this section.

There are two theoretical studies for the computation of AEA of OBrO that are worth mentioning. Xie and co-workers reported the electron affinities of bromine oxides calculated by a density functional theory method and the DZP++ basis set.[42] Their values for OBrO are in the range of 217−256 kJ/mol. The value obtained using BP86, 228 kJ/mol, is very close to the value reported in the present study, 229.5 kJ/mol. Alcamí and Cooper calculated BrO and $BrO_2$ and their anions using CASMP2, QCISD(T), and G2//QCI methods.[43] They used two basis sets of triple-$\zeta$ quality. The first was an all electron basis set, the split-valence triple-$\zeta$ basis developed by Schäfer et al.[44,45] The second employed the effective core potentials and the associated basis sets developed by Stevens et al.[46,47] The contraction scheme in the second basis set is different from that proposed by Stevens et al. Both basis sets were argumented by a set of (2d,1f) polarization functions.[48,49] Alcamí and Cooper calculated the AEA of OBrO using CASMP2 and QCISD(T) with the effective core potential basis set and G2/QCI with the all electron basis set. The calculated AEA values are 198, 219, and 251 kJ/mol for the CASMP2, QCISD(T), and G2/QCI methods, respectively. The CASMP2 and QCISD(T) values are smaller than ours by 31 and 10 kJ/mol, respectively, and the G2/QCI value is larger than ours by 22 kJ/mol. These differences of their values from ours seem to originate from the use of larger basis sets and the treatment of all electrons in electron correlation in the current study.

The deviation of the calculated value from the experimental value is 11.1 and 10.4 kJ/mol for OClO and OIO, respectively. Since these two errors are similar in magnitude and sign, the error in the calculated AEA of OBrO is expected to be comparable to these errors. The experimental AEA value of OBrO is estimated by correcting the average of the differences between the calculated values and the corresponding experimental values for the OClO and OIO molecules to the calculated value for OBrO. The estimated value is 240.1 kJ/mol. The same procedure was applied to estimate the AEAs of Br and BrO to justify our procedure. The deviation of the estimated value from the experimental value is −3.9 and −0.2 kJ/mol for Br and BrO, respectively. When this procedure was applied to X (X = Cl, Br, and I), XO (X = Cl, Br, and I), and OXO (X = Cl and I) of which the experimental AEAs are known, the uncertainties were calculated to be 11.1, 5.0, and 1.3 kJ/mol, respectively. There is no way to estimate the uncertainty of the estimated AEA for OBrO directly. But since the uncertainty is expected to be similar to that for OXO (X = Cl and I), it is reasonable to assume that the uncertainty is 1.3 kJ/mol. Thus, the estimated value for OBrO seems to be quite reliable.

**TABLE 3: The Calculated Enthalpy of Formation at 0 K (kJ/mol) of the OClO Anion**

| reaction | HF | MP2 | B3LYP | CCSD(T) | CCSD(T,Full) |
|---|---|---|---|---|---|
| | | | AE Basis | | |
| 1 | −86.7 | −116.8 | −101.5 | −102.2 | −104.6 |
| 2 | −93.3 | −109.0 | −101.0 | −96.9 | −100.3 |
| 3 | −109.4 | −104.1 | −106.0 | −97.8 | −101.7 |
| avg(1−3) | | −105.7(7.8) | −104.3(5.8) | −97.6(5.6) | −101.4(6.1) |
| | | | ECP Basis | | |
| 1 | −86.7 | −116.8 | −101.5 | −102.2 | −104.6 |
| 2 | −93.9 | −111.0 | −99.4 | −97.9 | −103.2 |
| 3 | −114.2 | −111.9 | −110.4 | −104.3 | −109.7 |
| avg(1−3) | | −111.9(5.1) | −105.5(8.8) | −99.8(6.4) | −107.6(6.8) |
| overall | | −109.7(6.3) | −104.9(6.0) | −98.7(5.6) | −104.8(6.5) |

**B. Enthalpies of Formation of the OXO Anions.** *$OClO^-$*. The experimental heat of formation of the OClO anion, $\Delta_f H_0^\circ(OClO^-) = -106.3(2.4)$ kJ/mol, is obtained from the experimental adiabatic electron affinity,[41] AEA(OClO) = 207.0(0.2) kJ/mol, and the experimental heat of formation, $\Delta_f H_0^\circ(OClO) = 100.7(2.4)$ kJ/mol. This value is used as an experimental benchmark. The $\Delta_f H_0^\circ(OClO^-)$ values obtained from reactions 1−3 using various computational models are listed in Table 3.

The three reactions seem to be fairly good for the cancellation of systematic errors. The calculated results obtained with the AE basis set are very similar to the corresponding results obtained with the ECP basis set. However, there is a noticeable difference between the AE and ECP results for reaction scheme 3. If the electronic structure calculations are performed with the ECP basis, some scalar relativistic effects are included through the relativistic effective potential, but some core-valence correlations at the CCSD(T,Full) level cannot be accounted for due to the frozen core approximation used to derive the effective core potential for Br and I atoms. The inclusion of the scalar relativistic effects induces a slight change in the molecular geometry. However, if the AE basis is employed, the core-valence correlation can be included but the scalar relativistic effects are completely neglected. Considering that good agreement between the AE and ECP results is observed for reaction scheme 2, in which the scalar relativistic effects are not expected, the scalar relativistic effects seem to be the major source of the difference between the AE and ECP results for reaction scheme 3.

The weighted averages of the enthalpy of formations calculated with the AE basis set are −105.7(7.8), −104.3(5.8), −97.6(5.6), and −101.4(6.1) kJ/mol for the MP2, B3LYP, CCSD(T), and CCSD(T,Full) methods, respectively. The corresponding results with the ECP basis set are −111.9(5.1), −105.5(8.8), −99.8(6.4), and −107.6(6.8) kJ/mol for the MP2, B3LYP, CCSD(T), and CCSD(T,Full) methods, respectively. The overall weighted averages of enthalpy of formations calculated with both sets are −109.7(6.3), −104.9(6.0), −98.7(5.6), and −104.8(6.5) kJ/mol for the MP2, B3LYP, CCSD(T), and CCSD(T,Full) methods, respectively.

The CCSD(T,Full) method is the most sophisticated one for the inclusion of the electron correlation and can be expected to provide the most accurate calculated values. The results obtained at the MP2 level are smaller than the corresponding ones at the CCSD(T,Full) level by about 5 kJ/mol, the B3LYP results are smaller than the CCSD(T,Full) results by about 2 kJ/mol, and the CCSD(T) results are larger than the CCSD(T,Full) values by about 5 kJ/mol. Among the MP2, B3LYP, and CCSD(T)

**TABLE 4: The Calculated Enthalpy of Formation at 0 K (kJ/mol) of the OBrO Anion**

| reaction | HF | MP2 | B3LYP | CCSD(T) | CCSD(T,Full) |
|---|---|---|---|---|---|
| | | | AE Basis | | |
| 4 | −47.6 | −90.0 | −68.1 | −77.3 | −76.4 |
| 5 | −54.2 | −82.2 | −67.6 | −71.9 | −72.1 |
| 6 | −70.3 | −77.4 | −72.7 | −72.9 | −73.5 |
| 7 | −60.6 | −87.3 | −73.5 | −86.7 | −82.5 |
| 8 | −67.7 | −80.1 | −73.5 | −81.9 | −78.7 |
| 9 | −67.6 | −85.8 | −74.1 | −87.3 | −83.6 |
| avg(4−6) | | −78.5(9.0) | −71.9(5.9) | −72.9(5.7) | −73.5(6.0) |
| avg(7−9)) | | −82.9(9.9) | −73.7(5.4) | −84.4(10.2) | −80.8(8.7) |
| avg(4−9) | | −80.3(9.0) | −72.7(5.6) | −75.1(7.7) | −75.5(7.3) |
| | | | ECP Basis | | |
| 4 | −45.4 | −86.0 | −71.0 | −74.9 | −72.6 |
| 5 | −52.6 | −80.3 | −68.9 | −70.6 | −71.1 |
| 6 | −72.9 | −81.1 | −79.9 | −77.0 | −77.7 |
| 7 | −57.8 | −81.3 | −77.9 | −83.4 | −75.7 |
| 8 | −65.6 | −76.1 | −76.3 | −79.6 | −74.8 |
| 9 | −63.6 | −80.7 | −77.2 | −85.0 | −80.5 |
| avg(4−6) | | −81.3(8.6) | −76.8(9.8) | −76.2(6.9) | −76.6(7.3) |
| avg(7−9)) | | −78.2(8.9) | −76.9(7.7) | −81.8(10.2) | −76.3(8.2) |
| avg(4−9) | | −79.8(8.6) | −76.9(8.1) | −77.6(7.7) | −76.5(7.2) |
| overall | | −80.0(8.5) | −73.9(6.3) | −76.1(7.3) | −76.0(7.0) |

methods, the B3LYP method provides the best results, since the B3LYP results are closer to the CCSD(T,Full) results.

The weighted average of the results calculated with the CCSD(T,Full)/AE level, −101.4(6.1) kJ/mol, is higher than the benchmark by 5.0 kJ/mol. The weighted average of the results calculated with the CCSD(T,Full)/ECP level, −107.6(6.8) kJ/mol, is very close to the benchmark. The excellent agreement between this value and the benchmark may be regarded as fortuitous because some of the core-valence correlations are neglected in the calculations with the ECP basis. Thus, the overall weighted average of results calculated at the CCSD(T,Full) level with both basis sets can be regarded to be the best value for the enthalpy of the formation. The overall average is −104.8(6.5) kJ/mol, which is in very good agreement with the benchmark.

*OBrO$^-$*. The experimental enthalpy of formation of the OBrO anion is estimated based on the estimated adiabatic electron affinity of OBrO, AEA(OBrO) = 240.1(1.3) kJ/mol, and the experimental enthalpy of formation of OBrO, $\Delta_{\mathrm{f}}H^{\circ}_{0}(\mathrm{OBrO}) = 173.4(4.3)$ kJ/mol.[27] The estimated value is $\Delta_{\mathrm{f}}H^{\circ}_{0}(\mathrm{OBrO}^-) = -66.7(4.5)$ kJ/mol. The calculated enthalpies of formation are listed in Table 4.

The six reactions were fairly effective in canceling systematic errors, but the calculated values depend on the reaction scheme employed to derive the enthalpy of formation. The reaction schemes were classified into two groups based on the different types of the isodesmic reactions. The first group, which consisted of reactions 4−6, does not utilize the experimental enthalpy of formation of OClO$^-$, while the second group, which consisted of reactions 7−9, utilizes it.

The weighted averages of $\Delta_{\mathrm{f}}H^{\circ}_{0}(\mathrm{OBrO}^-)$ calculated with the AE basis for the reactions in the first group are −78.5(9.0), −71.9(5.9), −72.9(5.7), and −73.5(6.0) kJ/mol for the MP2, B3LYP, CCSD(T), and CCSD(T,Full) methods, respectively, and the corresponding ones for the reactions in the second group are −82.9(9.9), −73.7(5.4), −84.4(10.2), and −80.8(8.7) kJ/mol for the MP2, B3LYP, CCSD(T), and CCSD(T,Full) methods, respectively. The results for the second group were always lower than the corresponding results for the first group. The differences between the results for both groups arise from the different type of reaction schemes and the different magnitude of the error of the experimental enthalpies of formation employed in each groups. It is noteworthy that the differences between the B3LYP results in both groups are smaller than those obtained with the other methods. The overall weighted averages with the AE basis are −80.3(9.0), −72.7(5.6), −75.1(7.7), and −75.5(7.3) kJ/mol for the MP2, B3LYP, CCSD(T), and CCSD(T,Full) methods, respectively.

The weight averages of $\Delta_{\mathrm{f}}H^{\circ}_{0}(\mathrm{OBrO}^-)$ calculated with the ECP basis for the reactions in the first group are −81.3(8.6), −76.8(9.8), −76.2(6.9), and −76.6(7.3) kJ/mol for the MP2, B3LYP, CCSD(T), and CCSD(T,Full) methods, respectively, while the corresponding averages for the reactions in the second group are −78.2(8.9), −76.9(7.7), −81.8(10.2), and −76.3(8.2) kJ/mol for the MP2, B3LYP, CCSD(T), and CCSD(T,Full) methods, respectively. The differences between the ECP results for the two groups are much smaller than those from the calculations with the AE basis and are negligible. The overall averages with the ECP basis are −79.8(8.6), −76.9(8.1), −77.6(7.7), and −76.5(7.2) kJ/mol for the MP2, B3LYP, CCSD(T), and CCSD(T,Full) methods, respectively. The overall averages calculated with the ECP basis are very similar to the corresponding AE results.

The trend in the weighted averages derived with the different computational methods is similar to the trend found in the calculated results for OClO$^-$. That is, the MP2 results were always lower than the corresponding CCSD(T,Full) results by about 5 kJ/mol, the B3LYP results were lower than the CCSD(T,Full) results by about 2 kJ/mol, and the CCSD(T) results were higher than the CCSD(T,Full) values by about 1 kJ/mol. However, the accuracy of the CCSD(T) results is improved so much that the CCSD(T) results are regarded to be the same as the CCSD(T,Full) results if their uncertainties are considered. The accuracy of the results obtained by the different methods increases in the order of the MP2, B3LYP, CCSD(T), and CCSD(T,Full) methods. The results obtained from the B3LYP and CCSD(T) calculations are satisfactory because the deviations of these results from the corresponding CCSD(T,Full) results are less than 4 kJ/mol.

The overall averages derived from the calculated results obtained with both basis sets for all the reactions are −80.0(8.5), −73.9(6.3), −76.1(7.3), and −76.0(7.0) kJ/mol for the MP2, B3LYP, CCSD(T), and CCSD(T,Full) methods, respectively.

The weighted averages derived at the CCSD(T,Full)/AE level for the first and second groups are smaller than the experimental value by 6.8 and 14.1 kJ/mol. Since the deviation of the weighted average of $\Delta_{\mathrm{f}}H^{\circ}_{0}(\mathrm{OClO}^-)$ calculated at the CCSD(T,Full)/AE level from the corresponding experimental value is so small and since the weighted average of $\Delta_{\mathrm{f}}H^{\circ}_{0}(\mathrm{OBrO}^-)$ for the first group is derived using the isodesmic reactions that are very similar to those for the derivation of the calculated $\Delta_{\mathrm{f}}H^{\circ}_{0}(\mathrm{OClO}^-)$ value, the accuracy of the calculated $\Delta_{\mathrm{f}}H^{\circ}_{0}(\mathrm{OBrO}^-)$ value can be expected to be very similar to the OClO$^-$ counterpart, but the deviation of calculated value for OBrO$^-$ from the experimental value is larger than that for OClO$^-$. The larger error in $\Delta_{\mathrm{f}}H^{\circ}_{0}(\mathrm{OBrO}^-)$ may be attributable to the error in the estimated electron affinity of OBrO$^-$, the derivation of the experimental enthalpy of formation, or both. Since the error in the estimated AEA of OBrO is expected to be similar in magnitude to the error for BrO, it is necessary to reinvestigate the experimental enthalpy of OBrO. If the difference between the calculated and experimental values for OBrO$^-$ is assumed to be the same as that for OClO$^-$ and correcting the difference for OClO$^-$ to the calculated value of OBrO$^-$, −76.0(7.0) kJ/mol, the experimental value for OBrO$^-$ is expected to be around −81 kJ/mol.

**TABLE 5: The Calculated Enthalpy of Formation at 0 K (kJ/mol) of the OIO Anion**

| reaction | HF | MP2 | B3LYP | CCSD(T) | CCSD(T,Full) |
|---|---|---|---|---|---|
| | | | AE Basis | | |
| 10 | −105.8 | −157.3 | −127.6 | −141.1 | −140.6 |
| 11 | −112.4 | −149.5 | −127.1 | −135.8 | −136.3 |
| 12 | −128.5 | −144.6 | −132.1 | −136.7 | −137.7 |
| 13 | −102.7 | −159.5 | −127.9 | −149.7 | −145.2 |
| 14 | −125.4 | −146.8 | −132.4 | −145.3 | −142.3 |
| 15 | −113.1 | −152.2 | −127.1 | −145.7 | −142.7 |
| avg(10−12) | | −146.7(13.4) | −131.1(6.2) | −136.9(8.2) | −137.7(8.6) |
| avg(13−15) | | −149.5(15.6) | −130.7(7.4) | −146.0(13.3) | −142.8(11.8) |
| avg(10−15) | | −147.8(13.7) | −131.0(6.2) | −139.2(10.2) | −139.4(9.9) |
| | | | ECP Basis | | |
| 10 | −95.2 | −146.8 | −121.4 | −131.1 | −128.5 |
| 11 | −102.4 | −141.1 | −119.4 | −126.8 | −127.1 |
| 12 | −122.7 | −141.9 | −130.3 | −133.2 | −133.6 |
| 13 | −87.3 | −141.3 | −117.4 | −133.1 | −125.1 |
| 14 | −114.8 | −136.4 | −126.2 | −135.2 | −130.2 |
| 15 | −95.3 | −135.3 | −116.1 | −130.0 | −124.1 |
| avg(10−12) | | −142.4(13.8) | −127.1(9.9) | −131.8(9.6) | −131.8(9.9) |
| avg(13−15)) | | −136.8(14.7) | −122.6(11.0) | −133.6(13.8) | −128.1(11.7) |
| avg(10−15) | | −139.8(14.3) | −125.4(9.2) | −132.3(10.7) | −130.4(10.3) |
| overall | | −144.1(14.0) | −129.1(7.2) | −136.1(10.4) | −135.0(10.3) |

*$OIO^-$*. The experimental enthalpy of formation of the OIO anion has been estimated based on the experimental adiabatic electron affinity of OIO,[16] AEA(OIO) = 248.6(0.8) kJ/mol, and the experimental enthalpy of formation of OIO, $\Delta_f H_0^\circ$(OIO) ≤134.7(4.3) kJ/mol.[9] The estimated value is $\Delta_f H_0^\circ(\mathrm{OIO}^-) \leq -113.9(4.4)$ kJ/mol. The calculated enthalpies of formation of $OIO^-$ are listed in Table 5.

As in the case of $OBrO^-$, the reaction schemes are classified into two groups. The first group consists of reactions 10−12, while the second group of reactions consists of reactions 13−15. Since the trends observed in the enthalpies of formation of $OIO^-$ calculated from different types of isodesmic reactions are very similar to those for $OBrO^-$, they need not be further discussed.

The overall averages with the AE basis are −147.8(13.7), −131.0(6.2), −139.2(10.2), and −139.4(9.9) kJ/mol for the MP2, B3LYP, CCSD(T), and CCSD(T,Full) methods, respectively. The overall averages with the ECP basis are −139.8(14.3), −125.4(9.1), −132.3(10.7), and −130.4(10.3) kJ/mol for the MP2, B3LYP, CCSD(T), and CCSD(T,Full) methods, respectively. When the results obtained with the different basis sets are compared, the results with the AE basis are smaller than the corresponding ECP results by at least 4 kJ/mol. The situation is similar to reaction 3 for $OClO^-$. As previously noted for $OClO^-$, the phenomena originate from the difference in the geometries of iodine species that are optimized with the two different basis sets. The geometry optimized with the ECP basis for iodine-containing molecules is much closer to the corresponding experimental value than the corresponding value with the AE basis.

The difference in the optimized geometries can be attributed to the incorporation of scalar relativistic effects in the calculations with the ECP basis. Since the ECP geometry for a molecule is much closer to the experimental one than to the AE geometry, the ECP results can be expected to be more accurate for energetics than the corresponding AE results. Thus, it may be more reasonable to count only the ECP results when the weighted average is taken. However, this approach was not used in the current study because the calculation with the ECP basis has some limitations due to the frozen core approximation and the treatment of only valence electrons of Br and I atoms in the CCSD(T,Full) calculations for electron correlation. There are no such limitations in the calculations with the AE basis. Since Irikura's procedure was designed to give larger and smaller weights for more and less accurate results, the overall weighted average of calculated results obtained from all the reactions with both basis sets can be expected to be the most appropriate enthalpy of formation to be compared with the experimental values. The overall weighted averages of the calculated results using both basis sets for all the reactions are −144.1(14.0), −129.1(7.2), −136.1(10.4), and −135.0(10.3) kJ/mol for the MP2, B3LYP, CCSD(T), and CCSD(T,Full) methods, respectively. The correct value is estimated to be around −140 kJ/mol based on the calculated value of $OIO^-$, −135.0(10.3) kJ/mol, and the difference between the calculated and experimental values for $OClO^-$. This is consistent with the experimental fact, $\Delta_f H_0^\circ(\mathrm{OIO}^-) \leq -113.9(4.4)$ kJ/mol.

**TABLE 6: The Calculated and Experimental Enthalpies of Formation at 0 K (kJ/mol) of the OXO (X = Cl, Br, and I) Radicals**

| | OClO | OBrO | OIO |
|---|---|---|---|
| calcd[a] | 102.2(6.5) | 164.1(7.1) | 113.6(10.3) |
| expt | 100.7(2.4)[b] | 173.4(4.3)[c] | <134.7[d] |

[a] The derived value in this work. [b] Reevaluated; see text. [c] From ref 27. [d] From ref 9.

The trend in the weighted averages obtained from the different computational methods is similar to the trend found in the calculated results for $OBrO^-$. However, the deviation of the B3LYP results from the CCSD(T,Full) results become somewhat larger so that the B3LYP values are larger than the CCSD(T,Full) by about 6 kJ/mol.

**C. Enthalpies of Formation of OXO.** The calculated enthalpies of formation for OXO (X = Cl, Br, and I) are obtained by correcting the adiabatic electron affinity of OXO[16] to the corresponding enthalpy of formation for the OXO anions obtained in the current study. The calculated values $\Delta_f H_0^\circ$ are 102.2(6.5), 164.1(7.1), and 113.6(10.3) kJ/mol for OClO, OBrO, and OIO, respectively, and are listed in Table 6, along with the experimental values.

The calculated $\Delta_f H_0^\circ$ value for OClO is in excellent agreement with the experimental value, 100.7(2.4) kJ/mol, suggesting that the present approach is sound and that the calculated values for other molecules obtained in this study are highly reliable.

The calculated $\Delta_f H_0^\circ$ value for OBrO is in excellent agreement with the previous calculated and estimated values.[27] Workman and Francisco performed their calculations at the CCSD(T)/6-311+G(3d,f) level for the Br + OBrO → 2BrO reaction and reported that the $\Delta_f H_0^\circ$(OBrO) = 144 kJ/mol.[50] Alcami and Cooper performed their calculations at the G2 level for the OBrO → BrO + O reaction and reported that the $\Delta_f H_0^\circ$(OBrO) = 156.9 kJ/mol.[19] Klemm et al. observed that the spin−orbit splitting of the chemical species involved in these two reactions should be taken into account. Their inclusion of the experimental spin−orbit splitting of Br and BrO improved 144 and 156.9 kJ/mol to 162.7 and 165.6 kJ/mol, respectively.[27] The corrected $\Delta_f H_0^\circ$ values are in excellent agreement with the present value. Chase's estimated value, $\Delta_f H_0^\circ$(OBrO) = 161.5(25) kJ/mol, obtained from trend analysis is in reasonable agreement with the current value. The calculated value for OBrO is smaller than the experimental value, 173.4(4.3), by 9.3 kJ/mol.[27] This large difference is perhaps attributable to the spin−orbit splitting of the ground state of the OBrO. However, no experimental or theoretical value is available for it. If the spin−orbit splitting of the ground state of OBrO is assumed to be the same as that for BrO, 968 $cm^{-1}$, although it is expected to be less than that of BrO, the correction of the estimated spin−orbit splitting on the enthalpy of formation is at most −5.8 kJ/

mol. However, the correction makes the difference between the calculated and experimental values larger. Therefore, it is necessary to reinvestigate experimentally the enthalpy of formation.

No experimental enthalpy of formation of OIO has been described in the literature. Bedjanian et al. investigated the kinetics of the IO + BrO reaction.[9] They identified Br and OIO in the products and the reaction IO + BrO → Br + OIO proceeding exothermically. The exothermicity of the channel implies that the $\Delta_f H_0^\circ$(OIO) is smaller than 134.7 kJ/mol. Chase estimated that $\Delta_f H_0^\circ$(OIO) = 162.7(25) kJ/mol based on the assumption that the ratio between the atomization energy of OXO and the dissociation energy of XO is identical for X = Cl and X = I; that is, $\Delta_{at} H_0^\circ(\mathrm{OIO})/D_0^\circ(\mathrm{IO}) = \Delta_{at} H_0^\circ(\mathrm{OClO})/D_0^\circ(\mathrm{ClO})$.[20] Klemm et al. estimated that $\Delta_f H_0^\circ$ (OIO) = 174(25) kJ/mol based on a similar assumption for X = Br and X = I; that is, $\Delta_{at} H_0^\circ(\mathrm{OIO})/D_0^\circ(\mathrm{IO}) = \Delta_{at} H_0^\circ(\mathrm{OBrO})/D_0^\circ(\mathrm{BrO})$.[27] Our value, $\Delta_f H_0^\circ$(OIO) = 113.6(10.3) kJ/mol, is consistent with Bedjanian's upper limit of $\Delta_f H_0^\circ(\mathrm{OIO}) \leq 134.7$ kJ/mol; however, it is smaller than two estimated values by 50−60 kJ/mol.

Misra and Marshall performed their calculations for $\mathrm{OIO^-} + \mathrm{ClO} \rightarrow \mathrm{OClO^-} + \mathrm{IO}$ at the approximate QCISD(T)/6-311+G(3d,f) (G2) level and derived $\Delta_f H_{298}^\circ(\mathrm{OIO^-}) = -171.9$ kJ/mol. By correcting the AEA(OIO) to $\Delta_f H_0^\circ(\mathrm{OIO^-})$, they obtained the $\Delta_f H_0^\circ$(OIO) = 80.4(15) kJ/mol.[18] Their value is smaller than ours by 33.2 kJ/mol. Most of this difference arises from the spin-contamination errors in the total energies of ClO and IO molecules and from the use of different value for the enthalpies of formation of OI and $\mathrm{OClO^-}$.

## 4. Summary

The enthalpies of formation of OXO (X = Cl, Br, and I) and their anions are calculated in the current study. The molecular geometries of these molecules are optimized at the levels of the Hartree−Fock (HF), the second-order Møller−Plesset perturbation theory (MP2), the density functional theory with the B3LYP hybrid functional (B3LYP), and the coupled cluster theory using single and double excitation with a perturbational treatment of triplet excitation (CCSD[T]) with two basis sets of triple-$\zeta$ plus polarization quality. The harmonic vibrational frequencies are calculated at the B3LYP level. The enthalpies of formation of OXO (X = Cl, Br, and I) and their anions are calculated at the HF, MP2, B3LYP, CCSD(T), and CCSD(T,Full) level by employing several isodesmic (or congeneric) reactions. The weighted averages and their associated uncertainties for the enthalpies of formation are derived for these molecules. The derived values are in excellent agreement with the available experimental values.

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