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Heat of Formation of OBrO: Experimental Photoionization Study[†]

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The appearance energy of BrO^+ from the dissociative ionization of OBrO was determined from the photoionization efficiency spectrum of BrO^+ over the wavelength range $\lambda = 90-122$ nm by using a discharge flow−photoionization mass spectrometer apparatus coupled to a vacuum- ultraviolet synchrotron radiation source. Bromine dioxide was generated in a flow tube reactor by first forming BrO via the reaction $O(^3P) + Br_2$ and then allowing the BrO to react on the cold flow tube wall. Species present in addition to OBrO were BrO, HOBr, Br_2O, and residual Br_2. The results are perturbed by a signal from BrO^+ formed by direct photoionization of BrO and by the dissociative ionization of Br_2O. It was possible to correct for these perturbations to obtain a clean appearance energy plot that yielded a threshold at $\lambda = 98.65 \pm 0.23$ nm. This gives $AE_{298}(BrO^+,OBrO) = 12.56_8 \pm 0.02_9$ eV. Taking known thermodynamic quantities, this result yields $\Delta_f H_0^o(OBrO) = 173.4 \pm 4.3$ kJ mol^{-1} (and $\Delta_f H_{298}^o(OBrO) = 163.9 \pm 4.4$ kJ mol^{-1}). This is the first experimental determination of the heat of formation of OBrO, and the present result is compared with those of previous estimates and recent calculations. In addition, computations (based on results from *ab initio* calculations) were performed to obtain $\Delta_f H_0^o(OBrO) = 164 \pm 8$ kJ mol^{-1}, which is in very good agreement with our experimental result. Also, a value for $\Delta_f H_0^o(OIO)$ of 174 ± 25 kJ mol^{-1} was estimated from a trend analysis that employed Chase's method (i.e., $\Delta_{at} H_0^o(OXO)/D_0^o(XO)$). Additionally, a comparison is made of recent photoelectron spectroscopic and photoionization mass spectrometric determinations of the ionization energies of BrO and OBrO.

Introduction

Halogen oxides are known to play an important role in atmospheric chemistry, especially in catalytic reaction cycles involved in stratospheric ozone depletion. The role of bromine oxides was established a decade ago,[1] and, more recently, the efficiency of bromine in this regard has been estimated to be about 50 times larger than that of chlorine.[2−4] An example of bromine reactions that are tentatively considered to be significant in this stratospheric chemistry are displayed in Figure 1. The potential importance of OBrO as a nighttime reservoir species was emphasized by its recent detection in the stratosphere by Renard et al.[5]

Although numerous studies have been reported[6−17] on the spectroscopic and thermodynamic properties of OBrO, there appear to be no experimental measurements of the heat of formation. In a recent review, Chase[13a] discusses two estimated values for $\Delta_f H_0^o(OBrO)$ that were reported by Cottrell[13b] and by Huie and Laszlo:[13c] 87 and 132 kJ mol^{-1}, respectively. Additionally, Chase[13a] estimates a value for $\Delta_f H_0^o$ (OBrO) of 161.5 ± 25 kJ mol^{-1} based on a trend analysis of $\Delta_f H_0^o(OClO)/D_0^o(ClO)$ and the accepted value of $D_0^o(BrO)$. Recent ab initio calculations reported by Workman and Francisco[16] and by Alcami and Cooper[17] give values for $\Delta_f H_0^o(OBrO)$ of 144 and 156.9 kJ mol^{-1}, respectively.

We report here the first measurement of the appearance energy (AE) for BrO^+ produced by the dissociative ionization of OBrO. From this AE value, we obtain an experimental determination of the heat of formation for OBrO.

In our prior PIMS study of OBrO,[10] the photoionization efficiency (PIE) spectrum of OBrO was measured to determine a value of 10.29 ± 0.03 eV for the adiabatic ionization energy (IE) of OBrO from analysis of the photoionization threshold at $\lambda = 120.49$ nm. In a more recent photoelectron spectroscopy (PES) study, Dyke et al.[11a] measured IE(OBrO) $= 10.26 \pm 0.02$ eV. The main conclusion of this thorough and insightful report is that the photoelectron band, observed in their previous PES work[11b] and assigned to BrO, is actually associated with the secondary product OBrO. This new result is an excellent confirmation of our IE measurement (IE(OBrO) $= 10.29 \pm 0.03$

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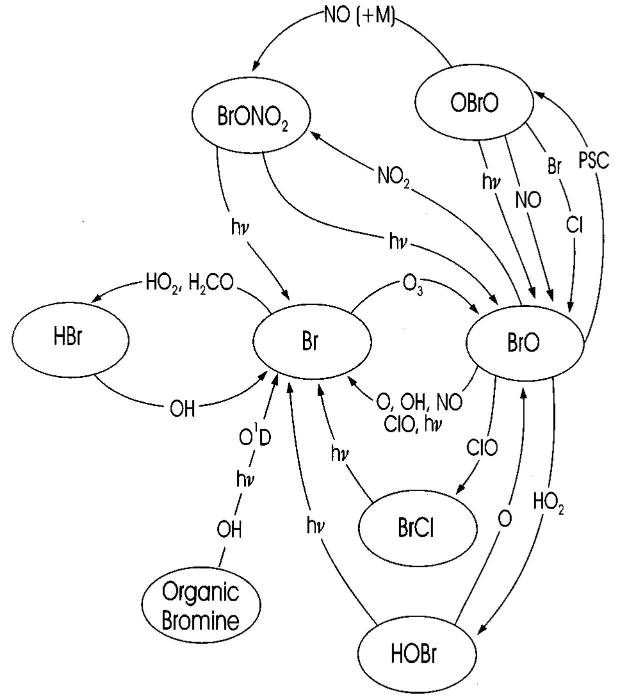

Figure 1. "Stratospheric bromine cycles" diagram summarizing the bromine reactions that are known or suspected to be important in the stratospheric destruction of ozone with an efficiency that may be 50 or more times larger than that of Cl. The arrows indicate the reactive conversion of bromine species that involve other molecular compounds or light (*hν*). In the diagram, M represents a "third body" collision partner and PSC stands for polar stratospheric clouds.

eV),[10] and, furthermore, it explains the contradiction between their earlier BrO result (IE = 10.29 eV)[11b] and our PIMS result (IE = 10.46 eV,[18] which we corrected to 10.48 eV in our OBrO paper).[10] Moreover, our PIMS results for IE(BrO)[10,18] were also brilliantly confirmed in the new PES study (10.46 eV)[11a] as well as in a recent calculation (10.45 eV).[11c]

Experimental Section

In the present investigation, experiments were performed by employing a discharge flow−photoionization mass spectrometry (DF−PIMS) apparatus coupled to the U-11 beamline on the vacuum-ultraviolet (vacuum-UV) ring at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The apparatus and procedures have been described in detail in previous publications.[10,18−27] As in our prior study,[10] OBrO was formed readily on the cold flow tube wall from gaseous BrO, which was a product of the $O(^3P) + Br_2$ reaction. The flow velocity was typically 1550−1600 cm s^{-1}, and the flow tube pressure was maintained at about 3 Torr with helium carrier gas. As before,[10] we estimate that about 5% of the O_2 was converted in the microwave discharge, and therefore $[O] \approx 5 \times 10^{12}$ atoms cm^{-3}. The Br_2 concentration was always in large excess at $(0.5-2.0) \times 10^{14}$ molecules cm^{-3}. The concentration of OBrO generated was estimated to be in the range of $10^{11}-10^{12}$ molecules cm^{-3}. In addition to OBrO, other species observed mass spectrometrically at an ionization energy of 12.4 eV (λ = 100.0 nm) were HOBr, BrO, and Br_2O plus residual Br_2.[10] It should be noted that the presence of HOBr requires sufficient mass resolution to avoid a contribution to the BrO^+ signal from the neighboring $HOBr^+$ ion and that this was accomplished in the present work. The gaseous mixture in the flow reactor was sampled as a molecular beam into the source chamber and subsequently into the photoionization region of the mass spectrometer. Ions were mass selected with an axially aligned quadrupole mass filter, detected with a channeltron/pulse preamplifier and counted for preset integration times. Measurements of PIE spectra (the ratio of ion counts/light intensity vs wavelength) were made using tunable vacuum-ultraviolet radiation at the NSLS. A monochromator with a normal incidence grating (1200 lines/mm) was used to disperse the vacuum-UV light. Since a LiF filter ($\lambda \geq 105$ nm) was not used, it was necessary to correct the PIE data for signal due to ionization by second-order light.[10,27,28] The intensity of the dispersed vacuum-UV light was monitored via a sodium salicylate coated window with an attached photomultiplier tube.

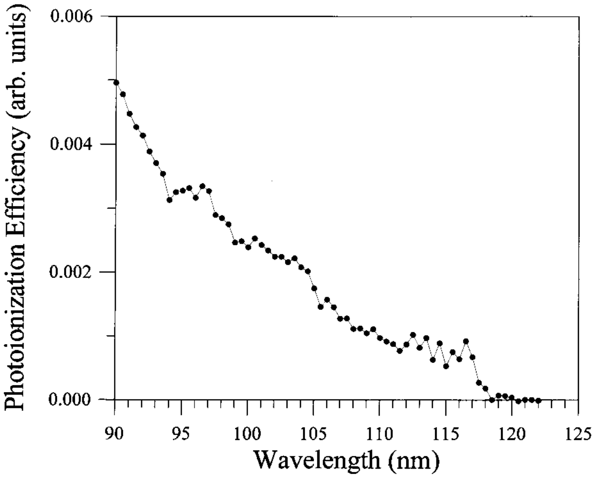

Figure 2. AE plot for the appearance of BrO^+ (uncorrected—see text) at $m/z = 95$ between $\lambda = 90.0$ and 122.0 nm at a nominal resolution of 0.2 nm and with 0.5 nm steps.

The conditions used in the present experiments were essentially the same as in our prior study[10] for two reasons: (1) the OBrO signal was maximized, and (2) the Br_2O signal was minimized. In several runs performed in the ambient temperature flow tube, mass spectra clearly displayed signal due to OBrO. However, the OBrO signal level in these runs was very low (only about 3% as large as for the low-temperature runs), and no further experiments were performed at ambient temperature.[10]

Helium (MG Industries, scientific grade, 99.9999%) and oxygen (MG Industries, 1.9% in scientific grade helium) were used as supplied. Bromine (Fluka, purissma grade, >99%) was outgassed by repeated freeze−pump−thaw cycles.

Results and Discussion

In the present study, the PIE spectrum of BrO^+, shown in Figure 2, was measured by combining data from several runs to obtain the appearance energy for the dissociative ionization of OBrO. The results were perturbed by a signal from BrO^+ that was formed in two additional ways: (1) by direct photoionization of BrO and (2) by the dissociative ionization of Br_2O that was formed in the flow reactor along with OBrO. The threshold for process 1 is evident around 118.0−118.5 nm, and that for process 2 is at 105−106 nm. By using PIE spectra for each perturbation, obtained under isolated conditions, it was possible to correct for both contributions and obtain a remarkably clean appearance energy plot (*vide infra*). The PIE spectra for BrO^+ due to direct photoionization of BrO[10,18] and dissociative ionization of Br_2O[24] were published in previous papers from this laboratory, and they are not reproduced here. Although HOBr was also present in this system (as mentioned in the Experimental Section), the observed BrO^+ signal was not due

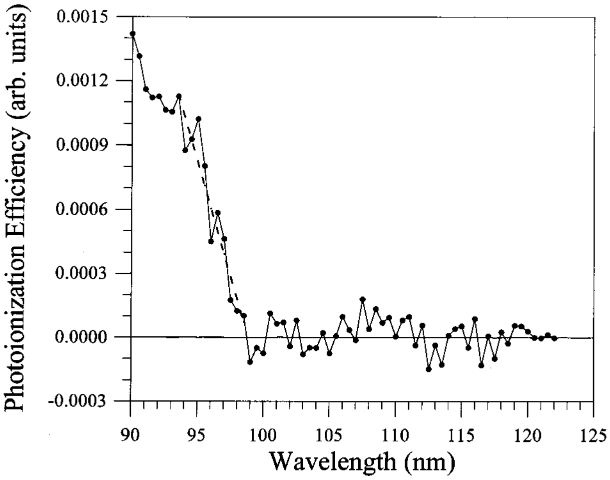

Figure 3. AE plot showing the photoionization threshold region for the appearance of BrO^+ from the dissociative ionization of OBrO (corrected for signal due to BrO and Br_2O—see text). The linear extrapolation of the spectrum to the baseline yields an onset at 98.65 nm ($AE_{298} = 12.56_8 \pm 0.02_9$ eV). The dashed line represents the linear fit of the data points (94.5−98.5 nm) that were utilized in this analysis. The fitting parameters are $Y = -2.41168 \times 10^{-4}X + 2.37901 \times 10^{-2}$, and the correlation coefficient of the fit, r^2, is 0.90903.

to dissociative ionization of HOBr because the process HOBr → BrO^+ + H is calculated to have a threshold above 14 eV.

A. Appearance Energy of BrO^+. The corrected PIE spectrum of BrO^+ at $m/z = 95$, formed via dissociative ionization of OBrO, is shown in Figure 3 over the wavelength range $\lambda = 90-122$ nm at 0.2 nm resolution and at 0.5 nm intervals. At the onset, BrO^+ formation displays a linear build-up that is expected for a process such as this.[29] Thus, the threshold was determined by making a simple extrapolation of the spectrum to the background at $98.65 \pm 0.22_9$ nm, which corresponds to an AE_{298} of $12.56_8 \pm 0.02_9$ eV.[30]

B. Determination of $\Delta_f H_0^\circ$(OBrO). The appearance energy determined here may be used to derive the heat of formation of OBrO. First, the AE must be corrected for the internal energy (E_i) present at room temperature in OBrO as discussed by Traeger and McLoughlin:[31−33]

$$\text{AE}_0(\text{BrO}^+,\text{OBrO}) = \text{AE}_{298} + E_i \quad (1)$$

$$= \text{AE}_{298} + (H_{298} - H_0)_{\text{OBrO}} - {}^5/_2RT \quad (2)$$

$$= 1217.8_5 \text{ kJ mol}^{-1} \qquad [12.62_2 \text{ eV}]$$

The uncertainty in this AE_0 value is estimated to be ±3.0 kJ mol^{-1}.[30] From this value for AE_0, $\Delta_f H_0^\circ$ (OBrO) can be computed using the heat of formation of BrO^+ (which was derived from the ionization energy for BrO (10.48 ± 0.02 eV)[10] and the heat of formation of BrO.[13a] For the dissociative ionization of OBrO to form BrO^+ (and O-atom, at zero K),

$$\text{OBrO} \rightarrow \text{BrO}^+ + \text{O},[\Delta_r H_0^\circ = \text{AE}_0] \quad (3)$$

the heats of formation are related to AE_0 by

$$\text{AE}_0 = \Delta_f H_0^\circ(\text{BrO}^+) + \Delta_f H_0^\circ(\text{O}) - \Delta_f H_0^\circ(\text{OBrO}) \quad (4)$$

Rearranging and using suitable $\Delta_f H$ values (from above and from ref 33)

$$\Delta_f H_0^\circ(\text{OBrO}) = \Delta_f H_0^\circ(\text{BrO}^+) + \Delta_f H_0^\circ(\text{O}) - \text{AE}_0 \quad (5)$$

$$= 1144.5 + 246.8 - 1217.9$$

$$\Delta_f H_0^\circ(\text{OBrO}) = 173.4 \pm 4.3 \text{ kJ mol}^{-1}$$

By applying the correction of 9.5 kJ mol^{-1} given in ref 13a for the integrated heat capacities of OBrO and the elements, this leads to a value for $\Delta_f H^\circ$ at 298 K,

$$\Delta_f H_{298}^\circ(\text{OBrO}) = 163.9 \pm 4.4 \text{ kJ mol}^{-1}.$$

The uncertainty associated with the present derivation of $\Delta_f H_0^\circ$ (OBrO) is conservatively estimated to be ±4.3 kJ mol^{-1}.[34] The value derived here for $\Delta_f H_0^\circ$(OBrO) from eqs 4 and 5 is a lower limit since AE_0 is an upper limit to $\Delta_r H_0^\circ$. The upper limit allows for the possibility of an energy barrier to the dissociative ionization of OBrO to BrO^+ + O. However, this dissociative ionization process is the lowest energy one (except for ion pair formation, i.e., $BrO^+ + O^-$), and it involves only a simple O−Br bond rupture. Since little or no energy barrier is expected, AE_0 should be a good measure of $\Delta_r H_0^\circ$.

C. Comparison of Reported Values for $\Delta_f H_0^\circ$(OBrO). The present value, $\Delta_f H_0^\circ$(OBrO) = 173.4 ± 4.3 kJ mol^{-1}, is compared with the previous estimated or calculated values listed in Table 1. The value estimated by Chase,[13a] 161.5 ± 25 kJ mol^{-1}, is in quite reasonable agreement with our experimental result, especially considering it was derived by means of a trend analysis. More importantly, two recent papers (Workman and Francisco[16] and Alcami and Cooper)[17] have performed calculations on the energies of reactions involving OBrO. However, neither paper included the corrections for the spin−orbit energies of the species involved. We can recompute the reaction energies and from these obtain an *ab initio* enthalpy of formation for OBrO.

Alcami and Cooper[17] performed calculations at the G2 level for

$$\text{OBrO} \rightarrow \text{BrO} + \text{O} \quad (6)$$

and reported a reaction energy of 224.3 kJ mol−[1] (which, evaluated relative to Chase's estimate,[13a] corresponds to $\Delta_f H_0^\circ$(OBrO) = 156.9 kJ mol−[1]). Workman and Francisco[16] performed calculations at the CCSD(T)/6-311+G(3df) level for reaction 7,

$$\text{Br} + \text{OBrO} \rightarrow 2\,\text{BrO} \quad (7)$$

and obtained an energy of −19.7 kJ mol^{-1} (and reported a value for $\Delta_f H_0^\circ$(OBrO) of 144 kJ mol^{-1}). BrO has a $^2P_{3/2}$ ground state and a $^2P_{1/2}$ component at 980 cm^{-1}.[33b] The ab initio energy provides an average of these two states. To derive the correct ground-state energy, we must therefore subtract this average energy from the ab initio energy. This yields a correction to the ab initio energy of (980)/2 = 490 cm^{-1} or 5.9 kJ mol^{-1}. Similarly, for Br the correction is 14.7 kJ mol^{-1} and for O-atom it is 0.9 kJ mol^{-1}. For the atoms, a *J*-degeneracy-weighted average was performed. We do not expect an appreciable spin−orbit splitting in the nonlinear OBrO radical. These numbers then provide the spin−orbit corrections to the reaction energies of 6.8 kJ mol^{-1} for reaction 6 and −3.0 kJ mol^{-1} for reaction 7. This yields reaction energies of 224.3 − 6.8 = 217.5 kJ mol^{-1} for reaction 6 and −19.7 − (−3.0) = −16.7 kJ mol^{-1} for reaction 7. By using enthalpies of formation (at 0 K) for Br, BrO, and O from Gurvich et al.[33b] of 117.933 ± 0.12, 133.428 ± 2.4, and 246.795 ± 0.1 kJ mol^{-1}, respectively, we obtain

TABLE 1: Comparison of Values for $\Delta_f H_0^o$(OBrO)

$\Delta_f\Delta_f H_0^o$(OBrO) (kJ mol^{-1})	ref	method/comment
87	Cottrell[13b]	derived from D(O−BrO)
132[a]	Huie and Lazlo[13c]	estd from $\Delta G(\mathrm{BrO_2(aq)})$
161.5 ± 25	Chase[13a]	estd from $1.94 \cdot D_0^0$(BrO)
144	Workman and Francisco[16]	ab initio calculation
162.7 ± 8	Workman and Francisco[16]	reevaluated (see text)
156.9[b]	Alcami and Cooper[17]	ab initio calculation
165.6 ± 8	Alcami and Cooper[17]	reevaluated (see text)
173.4 ± 4.3	this study	AE measurement

[a] Converted from the value at 298 K. [b] Evaluated relative to Chase.[13a]

predicted enthalpies of formation of OBrO as follows:

$$\text{for reaction 6:}\ 133.428 + 246.795 - \Delta_f H_0^o(\mathrm{OBrO}) = 217.5\ \mathrm{kJ\ mol^{-1}}$$

$$\text{or}\ \Delta_f H_0^o(\mathrm{OBrO}) = 162.7 \pm 2.4\ \mathrm{kJ\ mol^{-1}}$$

$$\text{for reaction 7:}\ (133.428) \times 2 - 117.933 - \Delta_f H_0^o(\mathrm{OBrO}) = -16.7\ \mathrm{kJ\ mol^{-1}}$$

$$\text{or}\ \Delta_f H_0^o(\mathrm{OBrO}) = 165.6 \pm 3.4\ \mathrm{kJ\ mol^{-1}}$$

The agreement between these two different calculations and reactions is satisfying, though perhaps it is fortuitously good. The stated uncertainties are for the experimental values; however, the systematic errors of the calculations are expected to be at least as large or larger than these. For comparison, the G2 atomization energy of BrO is within 7 kJ mol^{-1} of experiment.[35] By averaging the two calculated heat of formation values and by using uncertainties of ±7 kJ mol^{-1} for the reaction energies and ±3 kJ mol^{-1} for the experimental values (used for the spin−orbit corrections), we obtain a calculated heat of formation for OBrO of 164 ± 8 kJ mol^{-1}.

In summary, the heat of formation of OBrO was determined in this study by using the appearance energy of BrO$^+$ that was formed via dissociative ionization of OBrO. The values derived are as follows: $\Delta_f H_0^o(\mathrm{OBrO}) = 173.4 \pm 4.3$ kJ mol^{-1} and $\Delta_f H_{298}^o(\mathrm{OBrO}) = 163.9 \pm 4.4$ kJ mol^{-1}. From reevaluated *ab initio* calculations we obtained $\Delta_f H_0^o(\mathrm{OBrO}) = 164 \pm 8$ kJ mol^{-1}, which is in very good agreement with our experimental result, as is the value derived by Chase[13a] (161.5 ± 25 kJ mol^{-1}). With this level of agreement between experiment and theory, we conclude that the heat of formation of OBrO may now be considered to be well-established. The present results should be useful to kineticists and modelers who may need to evaluate the viability of reactions that involve the OBrO species. For example, the reaction of OBrO with bromine,

$$\mathrm{OBrO} + \mathrm{Br_2} \rightarrow \mathrm{Br_2O} + \mathrm{BrO} \qquad (8)$$

was suggested by Rattigan et al.[7a] to be involved in the thermal reaction of bromine with ozone. However, with a value of 173.4 kJ mol^{-1} for $\Delta_f H_0^o$(OBrO), reaction 8 is endothermic by about 40 kJ mol^{-1} and therefore it would probably be too slow ($k \le 1 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}) at ambient temperatures to be of any importance.

Finally, as was just noted above, the trend analysis result reported by Chase[13a] is in remarkably good agreement with the other values for $\Delta_f H_0^o$(OBrO), and it therefore seems quite reasonable to extend the analysis to include OIO. Although Chase[36] has already performed such a calculation to obtain a value of 162.7 ± 25 kJ mol^{-1}, we can utilize the results of the present study to refine the trend analysis. The ratio for $\Delta_{at} H_0^o(\mathrm{OIO})/D_0^o(\mathrm{IO})$ employed by Chase[36] was 1.94 (from the value derived for the Cl analog). However, the value for $\Delta_{at} H_0^o(\mathrm{OBrO})/D_0^o(\mathrm{BrO})$ obtained from the present heat of formation of OBrO is 1.89. By using this ratio, instead of 1.94, we derive a value for $\Delta_f H_0^o$(OIO) of 174 kJ mol^{-1} [37] with an assumed uncertainty of ±25 kJ mol^{-1}.

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(30) At the 2σ level, the uncertainty in the threshold measurement was estimated to be $\pm 0.22_9$ nm from a statistical analysis of the linear fits for different ranges of the data points. This corresponds to an uncertainty in AE_{298} of $\pm 0.02_9$ eV or $\pm 2.8_0$ kJ mol^{-1}. The uncertainty in the integrated heat capacity is estimated to be ± 1.00 kJ mol^{-1}; thus, the combined, root-sum-square (RSS) uncertainty in AE_0 is $\pm 2.9_7$ kJ mol^{-1} or in eV units, $\mathrm{AE}_0 = 12.62_2 \pm 0.03_1$.

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(34) The uncertainties in $\Delta_f H_0^\circ(\mathrm{BrO}^+)$, $\Delta_f H_0^\circ(\mathrm{O})$, and AE_0 are ± 3.1, ± 0.1, and ± 3.0 kJ mol^{-1}, respectively. Thus, the combined RSS uncertainty in $\Delta_f H_0^\circ(\mathrm{OBrO})$ is ± 4.3 kJ mol^{-1}. The uncertainty in $\Delta_f H_{298}^\circ(\mathrm{OBrO})$ is slightly larger due to the contribution of the integrated heat capacities

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(37) The ratio for $\Delta_{at}H_0^o(\mathrm{OBrO})/D_0^o(\mathrm{BrO})$—note that $\Delta_{at}H_0^o$ is the heat of atomization of OBrO—was computed from the present value for $\Delta_f H_0^o(\mathrm{OBrO})$ and values from ref 13a for $D_0^o(\mathrm{BrO})$ and ref 33 for $\Delta_f H_0^o(\mathrm{Br})$ and $\Delta_f H_0^o(\mathrm{O})$ as follows:

$$\begin{aligned}\Delta_{at}H_0^o(\mathrm{OBrO}) &= [\Delta_f H_0^o(\mathrm{Br}) + 2\Delta_f H_0^o(\mathrm{O})] - \Delta_f H_0^o(\mathrm{OBrO}) \\ &= 611.5 - 173.4 \\ &= 438.1\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

With $D_0^o(\mathrm{BrO}) = 231.42$ kJ mol^{-1} (from ref 13a), the ratio $\Delta_{at}H_0^o(\mathrm{OBrO})/D_0^o(\mathrm{BrO})$ is 1.89. The value for $\Delta_{at}H_0^o(\mathrm{OIO})$ was computed using $D_0^o(\mathrm{IO}) = 225.77$ kJ mol^{-1} from ref 36 and the ratio, 1.89, to obtain 426.7 kJ mol^{-1}. The value for $\Delta_f H_0^o(\mathrm{OIO})$ was finally computed as follows:

$$\begin{aligned}\Delta_f H_0^o(\mathrm{OIO}) &= [\Delta_f H_0^o(\mathrm{I}) + 2\mathrm{x}\ \Delta_f H_0^o(\mathrm{O})] - \Delta_{at}H_0^o(\mathrm{OIO}) \\ &= 600.7 - 426.7 \\ &= 174\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$