Thermochemistry of the Hypobromous and Hypochlorous Acids, HOBr and HOCl
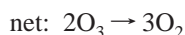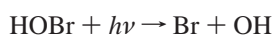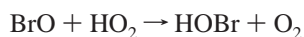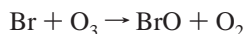
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The enthalpies of formation of HOBr and HOCl have been estimated by employing coupled cluster theory in conjunction with the correlation consistent basis sets and corrections for core-valence, relativistic, and anharmonic effects. We have employed three different reactions to estimate the $\Delta H°_{f,298}$(HOBr), namely, the atomization reaction and two homodesmic reactions. Our best estimation is $\Delta H°_{f,298}$ (HOBr) = −15.3 ± 0.6 kcal/mol and is very likely to lie toward the more negative values. The present value is 1.4 kcal/mol lower than the widely used experimental determination of Ruscic and Berkowitz (*J. Chem. Phys.* **1994**, *101*, 7795), $\Delta H°_{f,298}$(HOBr) > −13.93 ± 0.42 kcal/mol. However, it is closer to the more recent measurement of Lock et al. (*J. Phys. Chem.* **1996**, *100*, 7972), $\Delta H°_{f,298}$(HOBr) = −14.8 ± 1 kcal/mol. In the case of HOCl we have determined $\Delta H°_{f,298}$(HOCl) = −18.1 ± 0.3 kcal/mol, just in the middle of the two experimental values proposed, −17.8 ± 0.5 kcal/mol (JANAF), obtained from equilibrium constant measurements, and −18.36 ± 0.03 kcal/mol (Joens, J. A. *J. Phys. Chem. A* **2001**, *105*, 11041), determined from the measurements of the Cl− OH bond energy. If our conclusions are correct, several enthalpies of formation that have been determined by experimental chemists, Orlando and Burholder (*J. Phys. Chem.* **1995**, *99*, 1143), and theoretical chemists, Lee (*J. Phys. Chem.* **1995**, *99*, 15074), need to be revised, since a larger value was used for $\Delta H°_{f,298}$(HOBr). Employing the results obtained by Orlando and Burkholder for Br$_2$O we propose $\Delta H°_{f,298}$(Br$_2$O) = 24.9 ± 0.6 kcal/mol, and employing Lee's enthalpies of reaction we propose the following $\Delta H°_{f,298}$: for BrBrO, HBrO, ClOBr, ClBrO, BrClO, BrCN, BrNC, BrNO, BrON, FOBr, and FBrO, 39.5 ± 1, 41.0 ± 1, 22.7 ± 1.5, 34.2 ± 1.5, 40.9 ± 1.5, 43.7 ± 1.5, 80.1 ± 1.5, 22.3 ± 1, 46.2 ± 1, 17.3 ± 1.5, and 6.3 ± 1.5 kcal/mol, respectively. We expect that this work will stimulate new experimental measurements of the thermodynamic properties of HOBr and HOCl.

Introduction

Several investigations have confirmed that bromine catalytic cycles are far more efficient than their chlorine counterparts in the removal of stratospheric ozone. In the 80's it was proposed that HOBr participates in the stratospheric ozone depletion:[1,2]

$$Br + O_3 \rightarrow BrO + O_2$$

$$BrO + HO_2 \rightarrow HOBr + O_2$$

$$HOBr + h\nu \rightarrow Br + OH$$

$$OH + O_3 \rightarrow O_2 + HO_2$$

$$\text{net: } 2O_3 \rightarrow 3O_2$$

For that reason a survey of experimental[3−8] and theoretical[9−16] investigations has been performed to characterize hypobromus acid. One of the most important properties of HOBr is its enthalpy of formation, since it is very important to assess the role of HOBr in the catalytic cycles above-mentioned. The first estimation was performed in 1976 by Benson,[3] who suggested $\Delta H°_{f,298}$(HOBr) = −18.9 kcal/mol. We are aware of three experimental determinations of the $\Delta H°_{f,298}$(HOBr). Monks et al.[4] carried out a discharge flow-photoionization mass spectrometric study of HOBr and determined its ionization energy, suggesting a more positive enthalpy of formation, $\Delta H°_{f,298}$(HOBr) = −9 kcal/mol. Then 1 year later, Ruscic and

Berkowitz[5] determined the photoion yield curves of HOBr$^+$ and Br$^+$ from HOBr. The results obtained allowed them to estimate an upper limit to the Br−OH bond energy and suggested that $\Delta H°_{f,298}$ > −13.4 ± 0.5 kcal/mol. Finally, the most recent experimental determination is that of Lock et al.[6] They employed the information obtained in near threshold photodissociation dynamics to estimate the Br−OH bond energy and determined $\Delta H°_{f,298}$(HOBr) = −14.3 ± 1 kcal/mol, about 1 kcal/mol lower than the value proposed by Ruscic and Berkowitz.[5] The experimental determinations of the enthalpy of formation of HOBr that are based on the Br−OH bond energy require a precise determination of the $\Delta H°_{f,298}$(OH). However, the later property has presented important discrepancies. In 2002, Ruscic et al.[17] performed a combined experimental and theoretical work that suggested a new value for the enthalpy of formation of OH which is 0.5 kcal/mol lower than the generally accepted value (see ref 17 for a detailed discussion). If we employ the new value for the $\Delta H°_{f,298}$(OH) to correct the results of Berkowitz and Ruscic,[5] and Lock et al.,[6] we obtain the following $\Delta H°_{f,298}$ values for HOBr: −13.9 ± 0.5 and −14.8 ± 1 kcal/mol, Berkowitz and Ruscic[5] and Lock et al.,[6] respectively.

The problem of the enthalpy of formation of HOBr has also attracted the attention of several theoretical chemists. In 1994, McGrath and Rowland[11] determined $\Delta H°_{f,300}$(HOBr) = −14.2 ± 1.6 kcal/mol by employing G2 theory and two reactions, the atomization reaction and the homodesmic reaction HOBr + ClO → HOCl + BrO. The latter estimation is in good agreement with the experimental determination of Lock et al.[6] However, both measurements depend on some quantities that have

presented some discrepancies. As explained above, the experimental determination employed the controversial enthalpy of formation of the OH radical, and the theoretical estimation used G2 theory, which is a semiempirical methodology that presents some problems that have been partially solved in the more recent G3 approach. Moreover, as explained by Lee,[10] G2 theory is not designed to investigate the thermochemistry of molecules composed of third row atoms. Some of these drawbacks were considered by Glukhovtzev et al.[12] employing a modified version of G2 theory which included effective core potentials. Their estimation was $\Delta H°_{f,298}(HOBr) = -13.9$ kcal/mol. More recently, Hassanzadeh and Irikura[13] obtained the $\Delta H°_{f,298}(HOBr)$ as the average of nine different values obtained with nine reactions. The proposed value was $\Delta H°_{f,298}(HOBr) = -13.5$ kcal/mol. Finally, the most recent estimation that we are aware of is that of Joens,[14] who employed thermodynamic cycles to estimate the enthalpy of formation of HOBr. He used a value for the $\Delta H°_{f,298}(OH)$ which is nearly equivalent to the determined by Ruscic et al.[17] and derived $\Delta H°_{f,298}(HOBr) = -13.9 \pm 0.43$ kcal/mol and $\Delta H°_{f,298}(HOCl) = -18.36 \pm 0.03$ kcal/mol.[14,18–20] The estimation for HOCl is about 0.5 kcal/mol more negative than the value recommended by the JANAF tables.[55] The $\Delta H°_{f,298}$ included in the JANAF tables is based on the equilibrium constant determinations[21–23] of the reaction $Cl_2O + H_2O \rightarrow HOCl$ and at present time is the most accepted value for the $\Delta H°_{f,298}(HOCl)$. A proof of that is the inclusion of the latter value in the G297 test set.[60]

In view of the lack of a parameter-free estimation of the enthalpy of formation of HOBr and the discrepancies observed between the proposed values for $\Delta H°_{f,298}(HOCl)$ and because of the importance of the later properties in atmospherical and theoretical chemistry, we decided to estimate $\Delta H°_{f,298}(HOBr)$ and $\Delta H°_{f,298}(HOCl)$ by employing coupled cluster theory in conjunction with extrapolations to the complete basis set limit and including corrections for anharmonicities, core valence, and relativistic effects. The later procedure has been successfully employed to determine highly accurate enthalpies of formation of several molecules by us[24–27] and by other research groups.[28–36] Some of these theoretical values have been selected as reference values for several compilations such as the CRC Handbook of Physics and Chemistry.[37] In a previous work[25] we have evaluated the enthalpies of formation of other bromine oxides. The results obtained for the very difficult doublets BrO and OBrO were in excellent agreement with respect to experiment. In the case of BrO the estimated enthalpy of formation was 30.43 kcal/mol, to be compared with the experimental value 30.1 ± 0.4 kcal/mol, whereas for OBrO the result is also in good agreement with the experimental value, 39.14 ± 1 kcal/mol experiment vs. 39.85 kcal/mol theory. The differences between experiment and theory are larger for OBrO due to two reasons. First, because of the size of the molecule, the largest basis set employed was the aug-cc-pVQZ, and, second, the error in the experimental determination is larger than the observed for BrO. Quite recently Feller and co-workers[28] performed a landmark investigation of the thermochemistry of several halogen-containing molecules. The estimated enthalpies of formation for Br_2, HBr, and BrCl were 0.01, 0.2, and 0.3 kcal/mol far from experiment. Therefore, the procedure employed in the present article to investigate HOBr can provide accurate thermochemical information. We expect that the results obtained in this work will stimulate new experimental investigations of HOBr and HOCl.

Theoretical Methods

The traditional coupled cluster theory with single and double excitations and a perturbative treatment of triples excitations UCCSD(T) was employed.[38] For comparative purposes the UCCSDT calculations, which include iterative triple excitations, were performed.[39,40] The basis sets selected were the cc-pVXZ correlation consistent basis sets, X = D, T, Q, 5, 6.[41,42] We optimized geometries with all the basis set considered, except for the CCSD(T)/cc-pV5Z calculations. The later were performed at the cc-pVQZ geometry. The frozen core approximation was used for the coupled cluster calculations. Core−valence (CV) correlation effects were estimated as the difference between the full and frozen core CCSD(T) calculations employing the cc-pwCVQZ basis set[43,44] for HOCl and the cc-pwCVTZ for HOBr. It is important to notice that, in the full CCSD(T) calculations, we only correlated the next lower shell, i.e., the 3s, 3p, and 3d electrons of bromine, the 1s electron of oxygen, and the 2s and 2p electrons of chlorine. The 1s, 2s, and 2p electrons of bromine as well as the 1s of chlorine were kept frozen since they are expected to lie too low in energy. The extrapolation of the correlation energy to the complete basis set limit was performed with the two parameter extrapolation $E = B + C/L^3$, suggested by Halkier et al.[45] We carried out a separated extrapolation of the correlation energies from the HF energies. The later were determined with the cc-pV6Z basis set for HOCl. In the case of HOBr, we used the three-parameter extrapolation scheme $E = E_\infty + Ee^{-cx}$ (T, Q, 5) to estimate the HF/∞ energies.[46] We performed a test of the extrapolation with HOCl. The total atomization energy obtained at the HF/cc-pV6Z level of theory is 0.03 kcal/mol larger than the determined with the (T, Q, 5) three-parameter extrapolation. Thus, the extrapolation scheme does not overestimate the TAE.

Scalar relativistic effects (SR) were estimated at the DKCCSD-(T)/cc-pVQZ_DK level of theory,[47–48] where the cc-pVQZ_DK is a recontraction of the cc-pVQZ basis set for relativistic calculations.[50] The spin−orbit splitting for atoms were taken from Moore,[51] whereas zero point energies were taken from the work of Peterson.[52] All the CCSD(T) calculations were performed with Gaussian 03,[53] and the CCSDT jobs were carried out with ACESS II.[54] The basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, version 02/25/04.[61] The spin contamination in the doublet radicals discussed in this work, namely, ClO, BrO, and OBrO, was very small. Indeed, $\langle S^2 \rangle$ was always below 0.78.

Results and Discussion

Enthalpy of Formation of HOCl. To test our methodology in a system with a similar electronic structure, we decided to estimate the enthalpy of formation of the chlorine analogue of HOBr, namely HOCl. In Table 1 we report all the values employed to estimate the enthalpy of formation of HOCl. Our theoretical estimation, $\Delta H°_{f,298}(HOCl) = -18.1$ kcal/mol is in superb agreement with results suggested in the JANAF compilation,[55] −17.8 ± 0.5 kcal/mol, and by Joens,[14] −18.36 ± 0.03 kcal/mol. The deviation with respect to both values is the same, 0.3 kcal/mol. Jones considered the $\Delta H°_{f,298}(HOCl)$ derived by Wedlock et al.[18] and Barnes et al.,[19] obtained from measurements of the Cl−OH bond energy. The results determined in both experiments are in excellent agreement, $D_o = 19 288.8 \pm 0.6$ and $19 290 \pm 0.6$ cm^{-1}, Barnes et al.[19] and Wedlock et al.,[18] respectively. He used the average of the later values and employed the new $\Delta H°_{f,298}(OH)$. The enthalpy of formation proposed for HOCl by Joens is −18.36 ± 0.03 kcal/mol, in disagreement with that recommended by the JANAF[55] tables

TABLE 1: Estimated Enthalpies of Formation at 298 K for HOCl and HOBr (kcal/mol)

	HOCl	HOBr
equilibr atomization energies[a]	165.94	163.22
scalar relativistic[b]	0.28	0.7
spin−orbit[d]	1.06	3.73
core corr[c]	−0.32	−0.45
ZPE[f]	8.19	7.94
thermal corrs	2.44	2.47
final $\Delta H°_{f,298}$[b]	−18.07	−14.87

	$\Delta H°_{f,298}$(HOCl)	$\Delta H°_{f,298}$(HOBr)	ref
theor atomization	−18.1	−14.9	this work
theor homodesmic 1		−15.2 or −15.8[g]	this work
theor homodesmic 2		−15.2 or −15.8[g]	this work
proposed value	−18.1 ± 0.3	−15.3 ± 0.6[e]	this work
expt(298 K)	−17.8 ± 0.5		55
thermodynamic cycles	−18.36 ± 0.03	−13.9	14
expt(300 K)		−14.8 ± 1	6
expt(298 K)		>−13.93 ± 0.42	5
expt(298 K)		−9.0	4
theor(300 K) G2		−14.2 ± 1.6	11
theor G2(ECP)		−13.9	12
theor		−13.5	13

[a] Equilibrium total atomization energies at the CCSD(T)/∞ level. The HF, CCSD, and CCSD(T) contributions to total energies were extrapolated separately. See text for details. [b] Scalar relativistic correction to the enthalpy of formation evaluated at the DKCCSD(T)/cc-pVQZ_DK level of theory. [c] Core valence correction to the enthalpy of formation. Evaluated as the difference between the full and frozen core CCSD(T)/cc-pwCVQZ calculations for HOCl and CCSD(T)/cc-pwCVTZ for HOBr. [d] Atomic spin−orbit correction from ref 27. [e] Average of the three estimations, −14.9, −15.2, and −15.8 kcal/mol. [f] Zpe were taken from the work of Peterson.[59] [g] Both homodesmic reactions give the same equation $\Delta H°_{f,298}$(HOBr) = 2.6 + $\Delta H°_{f,298}$(HOCl). −15.2 kcal/mol is obtained if we employ the value recommended by the JANAF tables[55] for $\Delta H°_{f,298}$(HOCl); −17.8 ± 0.5 kcal/mol and −15.8 kcal/mol is obtained if we use the value recommended by Joens[13] for $\Delta H°_{f,298}$(HOCl) = −18.36 ± 0.3 kcal/mol.

by 0.56 kcal/mol. The value suggested in the JANAF tables was derived from the work of Kanuth et al.,[22] who measured the equilibrium constant of the reaction
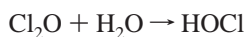
$$Cl_2O + H_2O \rightarrow HOCl$$

At least three groups[21,22] derived $\Delta H°_{f,298}$(HOCl) by employing the $Cl_2O + H_2O \rightarrow HOCl$ reaction, and the values obtained by the three groups are identical, −17.8 kcal/mol, only with small differences in the estimated error; we adopt the lowest error, ±0.5 kcal/mol. Our theoretical estimation for HOCl is bracketed by the values proposed by Joens[14] and the JANAF tables, lying in the middle of both values. The present calculations employing the atomization reaction do not allow us to decide which of the experimental results is the correct one.

We expect a minimal contribution of complete quadruples excitations in the estimated $\Delta H°_{f,298}$(HOCl) because of the error cancellation between the missing triple excitations in CCSD-(T) and the quadruple excitations.[56] Indeed, we have performed comparative CCSDT/cc-pVTZ calculations. The total atomization energy estimated at the CCSDT/cc-pVTZ level is 0.34 kcal/mol lower than that obtained by employing the CCSD(T)/cc-pVTZ methodology. Therefore, the error cancellation described in ref 56 is working and the CCSD(T) results are of nearly CCSDTQ quality. Thus, for an isovalent system we can expect a similar behavior.

Enthalpy of Formation of HOBr. *Atomization Reaction Results.* In Table 1 we report the computed data for HOBr

TABLE 2: Reaction Enthalpies for Reaction 1 and 2 and Derived $\Delta H°_{f,298}$(HOBr) (kcal/mol)

		$\Delta H°_{r,298}$	$\Delta H°_{f,298}$[a]	$\Delta H°_{f,298}$[b]
HCl + HOBr →	CCSD(T)/cc-pVQZ	10.73	−15.15	−15.71
HOCl + HBr	CCSD(T)/cc-pV5Z	10.77	−15.19	−15.73
	CCSD(T)/∞	10.81	−15.22	−15.76
ClO + HOBr →	CCSD(T)/cc-pVQZ	2.50	−14.39	−14.95
BrO + HOCl	CCSD(T)/cc-pV5Z	2.88	−14.77	−15.33
	CCSD(T)/∞	3.28	−15.17	−15.73

[a] JANAF value is employed for $\Delta H°_{f,298}$(HOCl) = −17.8 ± 0.5 kcal/mol.[55] [b] Joens values are employed for $\Delta H°_{f,298}$(HOCl) = −18.36 ± 0.03 kcal/mol.[14]

TABLE 3: Accepted Enthalpies of Formation of the Molecules Involved in the Homodesmic Reactions (kcal/mol)

molecule	$\Delta H°_{f,298}$		theor confirmation
HBr	−8.674 ± 0.038	JANAF[a]	−8.6[b]
HCl	−22.06 ± 0.024	JANAF[a]	−22.6,[b] −22.12[f]
HOCl	−17.8 ± 0.5	JANAF[a]	−18.10[c]
	−18.36 ± 0.03	Joens[e]	
ClO	24.192	JANAF[a]	24.78[d]
BrO	30.1 ± 0.4	JANAF[a]	30.43[d]

[a] Taken from ref 55. [b] Taken from ref 28. [c] Present work. [d] Taken from ref 25. [e] Taken from ref 14. [f] Taken from ref 36.

employing the atomization reaction. The scalar relativistic effects and spin−orbit splitting, essential to estimate the enthalpy of formation of HOBr, are 0.7 and 3.73 kcal/mol, respectively. The core valence correlation contribution evaluated with the cc-pwCVTZ basis set is −0.45 kcal/mol. Considering these corrections and the CCSD(T)/∞ enthalpy of formation, we estimate $\Delta H°_{f,298}$(HOBr) = −14.9 kcal/mol. Again, we have evaluated the contribution of complete triple excitations. At the CCSDT/cc-pVTZ level of theory, the estimated $\Delta H°_{f,298}$(HOBr) is 0.08 kcal/mol more positive than the obtained at the CCSD-(T)/cc-pVTZ level of theory. Thus, as observed for HOCl the error cancellation between the missing triple excitations and the quadruples is effective and the CCSD(T) results are of nearly CCSDTQ quality. It is important to notice that in some cases the later error cancellation does not work. We have found a few examples, the XOO and XO radicals, X = F, Cl, Br, and BN.[25,57] For these pathological cases, the CCSDT method predicted larger binding energies (more negative $\Delta H°_{f,298}$) than CCSD(T) and provided a better agreement with respect to experiment. The most serious case is that of FOO for which CCSDT predicted an $\Delta H°_{f,298}$ that is 1 kcal/mol lower than the determined with CCSD(T).[57] However, as expressed above, for HOBr the error cancellation is working and CCSD(T) provides results that are very close to the obtained if quadruple excitations are considered.

Homodesmic Reaction 1. We decided to perform two additional procedures to estimate the enthalpy of formation of HOBr. In both schemes we employed homodesmic reactions to minimize the contributions of high-order correlation effects, relativistic effects, problems in the extrapolations, etc. In the first one, we selected the following homodesmic reaction:

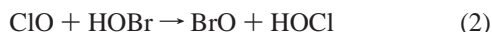$$HCl + HOBr \rightarrow HOCl + HBr \qquad (1)$$

In Table 2 we report the estimated enthalpies of reaction and enthalpies of formation at the CCSD(T) level for reaction 1 whereas in Table 3 are the accepted values for the enthalpies of formation of the molecules involved in reaction 1. The ultimate accuracy of the $\Delta H°_{f,298}$(HOBr) obtained by employing the homodesmic reaction 1 relies on the uncertainties of the enthalpies of formation of HCl, HBr, and HOCl.[14,55] We are

strongly convinced that these values are very accurate, with the exception of HOCl. Feller et al.[28] have corroborated the values for HBr and HCl (see Table 3). The deviation with respect to experiment is less than 0.1 kcal/mol for HBr. However for HCl it is larger, 0.54 kcal/mol. For that reason we searched in the literature for other theoretical investigations of the $\Delta H°_{f,298}$(HCl). Boese et al. employed W3 theory[36] to investigate the thermochemistry of several molecules that are included in the G297 test set.[60] The estimated enthalpy of formation for HCl was only 0.06 kcal/mol from experiment, confirming the experimental value. The main difference between the work of Feller et al.[28] and Boese et al.[36] is the core valence correction determined. The former investigators determined it as 0.7 kcal/mol; however, Boese et al.[36] obtained a much lower value of 0.19 kcal/mol. We have evaluated the core valence correction of HCl at the UCCSD(T)/cc-pwCVTZ level of theory. The result obtained is 0.23 kcal/mol, close to the value determined by Boese et al.;[36] thus, we believe that the uncertainty observed for HCl in ref 28 is due to the large core–valence correction. These results confirm that the $\Delta H°_{f,298}$(HCl) value reported in the JANAF tables is accurate enough (within 0.1 kcal/mol) to be used in this work.

With employment of the JANAF value for HOCl, the estimated enthalpies of formation at the CCSD(T)/cc-pVQZ and CCSD(T)/cc-pV5Z levels are −15.15 and −15.19 kcal/mol, respectively, in excellent agreement with our previous estimation of −14.9 kcal/mol. It is important to notice that reaction 1 presents a very small basis set dependence, confirming the error cancellations above-mentioned. The reader may ask what are the consequences of employing the $\Delta H°_{f,298}$(HOCl) suggested by Joens.[34] If we employ the later value, $\Delta H°_{f,298}$(HOCl) = −18.36 kcal/mol, the estimated $\Delta H°_{f,298}$ for HOBr becomes −15.78 kcal/mol, 0.83 kcal/mol larger that the obtained by employing the atomization reaction and much more negative than the experimental values suggested for HOBr.

Homodesmic Reaction 2. The final procedure selected to estimate $\Delta H°_{f,298}$(HOBr) employs the same homodesmic reaction as in the work of McGrath and Rowland:[11]

$$ClO + HOBr \rightarrow BrO + HOCl \qquad (2)$$

In Table 2 we report the estimated enthalpies of reaction for reaction 2 and enthalpies of formation at the CCSD(T) level, whereas in Table 3 are the accepted values for the enthalpies of formation of the molecules involved in reaction 2. The basis set dependence for reaction 2 is somewhat larger than that observed for reaction 1. The estimated enthalpies of formation at the CCSD(T)/cc-pVQZ and CCSD(T)/cc-pV5Z levels are −14.39 and −14.77 kcal/mol, respectively. Therefore, extrapolation to the ∞ limit is necessary. Employing the two-parameter extrapolation,[45] we obtain $\Delta H°_{f,298}$(HOBr) = −15.17 kcal/mol in excellent agreement with the result obtained with reaction 1 and also with that determined by employing the atomization reaction. As observed for reaction 1, if we employ the $\Delta H°_{f,298}$(HOCl) proposed by Joens, $\Delta H°_{f,298}$(HOBr) becomes −15.75 kcal/mol, again in excellent agreement with the value obtained by employing reaction 1 and $\Delta H°_{f,298}$(HOCl) proposed by Joens. It is important to note that we have considered the scalar relativistic and core valence effects for reactions 1 and 2 as well as spin–orbit splitting for the ClO and BrO radicals[58,59] in reaction 2. In both cases, the net effect of these corrections changes the estimated enthalpy of formation less than 0.1 kcal/mol, showing that it was not necessary to consider them to estimate $\Delta H°_{f,298}$(HOBr) when we use homodesmic reactions. All the data and corrections for the ClO and BrO radicals have

been taken from ref 25 (except the spin–orbit splitting[58,59]), where the enthalpies of formation of these two molecules were investigated.

Proposed Value for $\Delta H°_{f,298}$(HOBr). There are some potential sources of error in our estimation. In the procedure that employed the atomization reaction the most important problems are the following: (a) Only cc-pwCVTZ basis sets are used to estimate the core valence correction. Considering our previous works[24–27] we can expect a variation of 0.1–0.2 kcal/mol if a cc-pwCVQZ basis set is used. (b) There is second-order spin–orbit splitting. It is expected that the latter effect lowers the enthalpies of formation,[28] increasing the deviation with respect to experiment.[28] (c) There is the effect of quadruple excitations. It is expected to be minimal because the CCSDT calculations confirmed that there is an error cancellation between the missing triple excitations and the quadruples. Moreover, for nearly all the molecules for which CCSDTQ calculations are available,[56,36] the inclusion of the latter effect increased the binding energies. Therefore, if the CCSDTQ method is employed to estimate $\Delta H°_{f,298}$(HOBr), the result will be more negative, increasing the discrepancies with respect to experiment. (d) There are small errors in the extrapolation scheme employed.

We are strongly convinced that the errors b and c are the most problematic, but they going to decrease the $\Delta H°_{f,298}$(HOBr); errors a and d are going to be very small, 0.1–0.2 kcal/mol, but we cannot predict the effect on the estimated $\Delta H°_{f,298}$(HOBr). A final confirmation of these ideas is provided by the results obtained by employing the homodesmic reactions. When we employ the latter reactions to estimate enthalpies of formation, the errors cancel each other. Thus, if our ideas are correct (that the errors should decrease the enthalpy of formation of HOBr), the enthalpies of formation derived from homodesmic reactions should be more negative than those obtained from the atomization reaction. Indeed, we have seen the latter behavior, and we obtained −14.9 kcal/mol from atomization reactions and −15.2 and −15.8 kcal/mol from homodesmic reactions. Therefore, it is 100% sure that the errors are going to lower the enthalpy of formation of HOBr, increasing the deviation with respect to experiment. The main problem with homodesmic reactions is that the ultimate accuracy is determined by the uncertainies of the enthalpies of formation of the molecules considered. In this work all the enthalpies of formation involved in reactions 1 and 2 have been double checked by theoretical calculations. The only enthalpy of formation that presents problems is that of HOCl, but we have shown that if the $\Delta H°_{f,298}$(HOCl)-proposed Joens[14] value is correct and that proposed by the JANAF tables is not, $\Delta H°_{f,298}$(HOBr) will be more negative increasing the deviation with respect to experiment by 0.56 kcal/mol. Finally, what is more important, both homodesmic reactions give the same value

$$\Delta H°_{f,298} (HOBr) = 2.6 + \Delta H°_{f,298}(HOCl)$$

and indication of the robustness of the procedure. Employing two independent and different procedures, i.e., that based on the atomization reaction and the other based on homodesmic reactions, we have obtained three values for $\Delta H°_{f,298}$(HOBr), −14.9, −15.2, and −15.8 kcal/mol. The spread of the values is small, 0.80 kcal/mol, and most of the uncertainty is because of the problems in $\Delta H°_{f,298}$(HOCl). We propose a value for $\Delta H°_{f,298}$(HOBr) which is the average of the three results obtained: $\Delta H°_{f,298}$(HOBr) = −15.3 ± 0.6 kcal/mol. The $\Delta H°_{f,298}$ value is 0.5 and 1.4 kcal/mol lower than the experimental determinations of Lock et al.[6] and Rusic et al.,[5] respectively. It is important to note that at the present time the

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accepted value is the determined by Ruscic and Berkowitz,[5] $\Delta H°_{f,298}(HOBr) > -13.9 \pm 0.5$ kcal/mol.

Thermochemistry of Related Bromine-Containing Molecules. The enthalpy of formation of HOBr has been employed in several works to estimate the thermodynamic properties of other bromine-containing molecules which are very important in stratospheric chemistry. Orlando and Burkholder[15] measured the equilibrium constant for the reaction

$$Br_2O + H_2O \rightarrow 2HOBr$$

to estimate the enthalpy of formation of Br_2O. The value was constrained to the range 27−38 kcal/mol on the basis of the proposed values for $\Delta H°_{f,298}$ (HOBr). Employing the result obtained in the present work and the relationship derived by Orlando and Burkholder,[15] $\Delta H°_{f,298}(Br_2O) - 2\Delta H°_{f,298}(HOBr)$ = 55.5 kcal/mol, we propose $\Delta H°_{f,298}(Br_2O) = 24.9 \pm 0.6$ kcal/mol. The other work that employed the enthalpy of formation of HOBr is that of Lee.[9] Indeed, Lee pointed out in the conclusion that the accuracy of the proposed enthalpies of formation depends on the reliability of the experimental $\Delta H°_{f,298}$-(HOBr). Since Lee employed the $\Delta H°_{f,298}$(HOBr) suggested by Ruscic and Berkowitz, all the values obtained by Lee are affected. For example, in the case of Br_2O, the value obtained by Lee was 29.1 kcal/mol, 4.2 kcal/mol larger than that obtained if our value for HOBr is employed. For the remaining molecules investigated by Lee,[10] the enthalpy of formation of BrBrO is obtained by employing the isomerization enthalpy $Br_2O \rightarrow$ BrBrO, 14.6 kcal/mol,[10] and $\Delta H°_{f,298}(BrBrO) = 39.5 \pm 0.6$ kcal/mol, whereas for HBrO, ClOBr, ClBrO, BrClO, BrCN, BrNC, BrNO, BrON, FOBr, and FBrO their enthalpies of formation are reduced by 1.9 kcal/mol giving the $\Delta H°_{f,298}$ values 41.0 ± 1, 22.7 ± 1.5, 34.2 ± 1.5, 40.9 ± 1.5, 43.7 ± 1.5, 80.1 ± 1.5, 22.3 ± 1, 46.2 ± 1, 17.3 ± 1.5, and 6.3 ± 1.5 kcal/mol, respectively. It is important to notice that the enthalpies of formation of BrCN, BrNC, ClBrO, BrClO, and ClOBr are affected by $\Delta H°_{f,298}$(HOCl). For that reason larger error bars were considered.

Conclusions

The enthalpies of formation of HOBr and HOCl have been estimated by employing coupled cluster theory in conjunction with the correlation consistent basis sets and corrections for core−valence, relativistic, and anharmonic effects. We have employed three different reactions to estimate $\Delta H°_{f,298}$(HOBr), namely, the atomization reaction and two homodesmic reactions. Our best estimation is $\Delta H°_{f,298}(HOBr) = -15.3 \pm 0.6$ kcal/mol and is very likely to lie toward the more negative values. The present value is 1.4 kcal/mol lower than the widely used experimental determination of Ruscic and Berkowitz, $\Delta H°_{f,298}$-(HOBr) > -13.93 ± 0.42 kcal/mol. However, it is closer to the more recent measurement of Lock et al., $\Delta H°_{f,298}(HOBr)$ = -14.8 ± 1 kcal/mol. In the case of HOCl we have determined $\Delta H°_{f,298}(HOBr) = -18.1 \pm 0.5$ kcal/mol, just in the middle of the two experimental values proposed, -17.8 ± 0.5 kcal/mol (JANAF), obtained from equilibrium constant measurements, and -18.36 ± 0.03 kcal/mol (Joens), determined from measurements of the Cl−OH bond energy. If our conclusions are correct, several enthalpies of formation that have been determined by experimental chemists, Orlando and Burholder, and theoretical chemists, Lee, need to be revised, since a larger value was used for $\Delta H°_{f,298}$(HOBr). Employing the results obtained by Orlando and Burkholder for Br_2O, we propose $\Delta H°_{f,298}(Br_2O) = 24.9 \pm 0.6$ kcal/mol, and employing Lee's

enthalpies of reaction, we propose the following $\Delta H°_{f,298}$ values: for BrBrO, HBrO, ClOBr, ClBrO, BrClO, BrCN, BrNC, BrNO, BrON, FOBr, and FBrO, 39.5 ± 1, 41.0 ± 1, 22.7 ± 1.5, 34.2 ± 1.5, 40.9 ± 1.5, 43.7 ± 1.5, 80.1 ± 1.5, 22.3 ± 1, 46.2 ± 1, 17.3 ± 1.5, and 6.3 ± 1.5 kcal/mol, respectively. We expect that the present work will stimulate new experimental measurements of the thermodynamic properties of HOBr and HOCl.

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