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Accurate Enthalpies of Formation of Alkali and Alkaline Earth Metal Oxides and Hydroxides: Assessment of the Correlation Consistent Composite Approach (ccCA)

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Computing the enthalpies of formation for alkali metal and alkaline earth metal oxides (M_xO) and hydroxides [$M(OH)_n$] using the Gaussian-*n* (G*n*) and Weismann-*n* (W*n*) ab initio model chemistries is difficult due to an improper treatment of core-valence electron correlation effects. Using a new model chemistry called the correlation consistent Composite Approach (ccCA), enthalpies of formation were determined for eight different alkali/alkaline earth metal oxides and hydroxides. Unlike the G*n* and W*n* model chemistries, which must be modified to properly account for core-valence electron correlation, the standard implementations of the ccCA provide acceptable results, and all enthalpies of formation obtained with the ccCA are within the accepted range of recommended values.

Introduction

The oxides and hydroxides of alkali and alkaline earth metals are ubiquitous molecules with everyday uses that range from antacids (magnesium oxide) to soap manufacture (sodium hydroxide).[1] Experimental thermochemical studies for these molecules can be challenging because of their low volatility and high reactivity in the gas phase.[2−5] Because of this, ab initio procedures are useful tools in determining thermochemical and spectroscopic information about these molecules.

Enthalpies of formation ($\Delta H_f^{298.15\ K}$) have been computed in previous studies using standard ab initio model chemistries.[6−8] Surprisingly, the alkali and alkaline earth metal oxides and hydroxides have proven to be a significant challenge for the standard composite methods. In the 1999 study by Schulz et al.[7] it was determined that the G2 method[9] failed to accurately predict enthalpies of formation for 12 metal oxides and hydroxides. Though the G*n* methods are expected to predict enthalpies of formation (ΔH_f) to within 4−8 kJ mol^{-1} of experimental values, the G2-calculated ΔH_f values deviated greatly from experiment; for example, the difference between theory and experiment was 368 kJ mol^{-1} for CaO! Modifying the G2 methods to incorporate core-valence correlation drastically improved the agreement with experiment, but deviations from experiment still ranged between 16 and 42 kJ mol^{-1}, even with expensive all-electron coupled cluster computations. The more recent study by Sullivan et al.[8] using the G3,[10] G3X,[11] W1, and W2[12] composite methods did show better overall results, although Na_2O, MgO, and $Ca(OH)_2$ still presented a challenge depending on the choice of relaxed valence space. Only when G3X and W2 methods were modified to include core-valence or all-electron computations did all of the ΔH_f values consistently lie within the recommended experimental error bars.

The application of standard model chemistry implementations on s-block metals has been shown, in general, to be difficult. Petrie created a modified G2 method called “G2(thaw)” to account for core-valence correlation in studies of sodium cation affinities.[13−16] However, further investigations have resulted in additional G*n* modifications with widely varying accuracy.[15,16] Ma and co-workers have suggested that deficiencies in the G*n* treatments of s-block molecules could be alleviated by adding geometry corrected counterpoise (GCP) corrections.[17−20] By necessitating a correction for basis set superposition error (BSSE), another nonstandard implementation of G*n* theories (G3-GCP) was created. In this case, the BSSE correction is inconsistent from a theoretical point of view, as the high-level correction of G*n* largely corrects for an incomplete basis set.[21]

Recently, our group[21] has formulated a new model chemistry, called the correlation consistent Composite Approach (ccCA), that reliably reproduced energies with chemical accuracy (ca. ±4 kJ mol^{-1}) for a test set of energies. DeYonker and co-workers[22] have since made significant improvements to the original ccCA algorithm, and they successfully applied the ccCA to the G3/99 test set.[23] For the 376 atomic and molecular energies within the G3/99 training set, the ccCA has shown to be at least as reliable as the G3X model chemistry, but unlike G3X, *ccCA does not use any empirical parameters*. As the s-block metal oxides and hydroxides generally seem to present a difficult challenge for sophisticated model chemistries, we wish to assess the utility of the ccCA for these species. Thus, in this research, the ccCA has been applied to first- and second-row alkali and alkaline earth metal oxides (Li_2O, Na_2O, BeO, and MgO) and hydroxides (LiOH, NaOH, $Be(OH)_2$, and $Mg(OH)_2$).

Computational Methods

Standard ab initio molecular orbital theory and density functional theory computations were carried out with the GAUSSIAN03 and MOLPRO 2002.6 program packages. Structures were optimized at the B3LYP level of theory with the 6-31G(2df,p) basis sets. Harmonic vibrational frequencies scaled by a factor of 0.9854 were also computed using B3LYP/6-31G(2df,p) at the equilibrium geometries to obtain the required zero-point vibrational energies (ZPVE) and enthalpy corrections. Single point energies were then calculated with the standard ccCA formalism as given in ref 22. Compared to the G*n* methods that employed the Pople-style contracted Gaussian basis

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TABLE 1: Computed Equilibrium Structures of Alkali and Alkaline Earth Metal Oxides and Hydroxides

		geometric parameters[a]			
molecule	geometric level of theory	r_e(M−O)	r_e(O−H)	−MOH	−OMO
BeO	B3LYP/6-31G(2df,p)	1.324			
	expt[b]	$r_e = 1.3309$			
MgO	B3LYP/6-31G(2df,p)	1.736			
	expt[b]	$r_e = 1.749$			
Li_2O	B3LYP/6-31G(2df,p)	1.620		180.0	
	expt[c]	$r_0 = 1.606$		180.0	
Na_2O	B3LYP/6-31G(2df,p)	1.984		180.0	
LiOH	B3LYP/6-31G(2df,p)	1.581	0.951	180.0	
	expt[d]	$r_e = 1.5816(10)$	$r_e = 0.9691(21)$	180.0	
NaOH	B3LYP/6-31G(2df,p)	1.914	0.954	180.0	
	expt[d]	$r_e = 1.95(2)$		180.0	
$Be(OH)_2$	B3LYP/6-31G(2df,p)	1.420	0.954	127.3	176.8
$Mg(OH)_2$	B3LYP/6-31G(2df,p)	1.779	0.952	142.6	180.0

[a] Bond distances are listed in angstroms, and bond angles are in degrees. [b] Reference 36. [c] Reference 38. [d] Reference 37.

sets to compute single point energies at the optimized geometries, the ccCA method uses correlation consistent polarized valence basis sets (cc-pV*X*Z, where *X* is the zeta level of the basis set). These basis sets, originally developed by Dunning,[24] were constructed by systematically expanding the higher angular momentum functions in shells. Correlation consistent basis sets exist for first-, second-,[25] and third-row elements,[26] and have been augmented with diffuse functions (aug-cc-pV*X*Z).[27,28] They have also been modified to account for core-valence electron correlation (cc-pCV*X*Z).[29] Newly optimized (aug)-cc-p(C)V*X*Z basis sets for Li, Be, Mg, and Na were obtained from Peterson.[30] For this study, new second-row core-valence basis sets augmented with tight-d functions [aug-cc-pCV(*X*+d)Z] have also been used.[31]

The most accurate formulations of the ccCA employ MP2 extrapolations to the complete basis set limit (CBS).[21,22,31] The ccCA reference energy using the Peterson mixed exponential/Gaussian function extrapolation scheme[33] (called ccCA-P) with the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets, is determined using the formula

$$E(x) = A_{\mathrm{CBS}} + B\exp[-(x-1)] + C\exp[-(x-1)^2] \quad (1)$$

while reference energies with the two-point Schwartz $1/(l_{\max}{}^4)$ scheme[34,35] (called ccCA-S4) using aug-cc-pVTZ and aug-cc-pVQZ energies are determined using the formula

$$E(l_{\max}) = E_{\mathrm{CBS}} + \frac{B}{\left(l_{\max} + \frac{1}{2}\right)^4} \quad (2)$$

The MP2 CBS reference energies are then computed with additive effects of higher order electron correlation, core-valence correlation, and treatment of scalar relativistic effects. For a complete discussion of the various additive corrections involved in computing the ccCA energies, see ref 22. It is important to note here that the ccCA CBS extrapolations will eliminate any basis set superposition error, and no counterpoise corrections should be necessary for a proper treatment of s-block molecules.

Results and Discussion

Molecular structures are compared with known experimental data[36−38] in Table 1. At the B3LYP/6-31G(2df,p) levels of theory, all molecules except $Be(OH)_2$ are expected to be linear. Computed equilibrium structures match experimental data well, with the largest difference of 0.04 Å occurring for the Na−O bond length in the optimization of NaOH.

TABLE 2: Computed Enthalpies of Formation for ccCA Procedures (in kJ mol^{-1})[a]

molecule	ccCA-P	ccCA-S4	recommended[b]
BeO	126.9	126.6	+130 ± 12
MgO	141.4	140.8	+142 ± 10
Li_2O	−160.6	−160.6	−157 ± 5
Na_2O	−24.2	−24.6	−25 ± 5
LiOH	−243.9	−244.0	−239 ± 5
NaOH	−192.7	−193.0	−189 ± 5
$Be(OH)_2$	−634.2	−635.2	−632 ± 7
$Mg(OH)_2$	−551.9	−552.2	−547 ± 5

[a] All cited and computed enthalpies of formation used in this study are determined at 298.15 K. [b] From ref 8.

The implementations of the ccCA, G*n*, and W*n* procedures were compared with the recommended enthalpy of formation values given by Sullivan and co-workers[8] since the experimental data had a wide range of results, often with large error margins. These recommended values were calculated as weighted averages based on a double weighting of W2C//ACQ and a single weighting of G3[CC](dir,full) as the former method was considered to be more accurate.

As all ΔH_f values are within the error bars of the recommended values from Sullivan, it is apparent that the ccCA-P and ccCA-S4 algorithms (Table 2) have produced acceptable values for the enthalpies of formation of the eight s-block molecules investigated in this study. In fact, when comparing the ccCA with standard implementations of other composite methods (Table 3), only the enthalpies determined by the ccCA fell within error margins for all evaluated molecules. With G3X, only two of the eight molecules are within the error bars, with $Mg(OH)_2$ having a deviation of 39 kJ mol^{-1} from experiment. The original implementation of the W2 method also has trouble with this set of molecules. Only one W2-predicted enthalpy of formation (NaOH) is inside the recommended uncertainties, while the W2-predicted ΔH_f for $Mg(OH)_2$ has a deviation that is 152 kJ mol^{-1}.

From the data in Table 3, it can be seen that the ccCA is the most reliable of the unmodified methods in determining enthalpies for this test set of alkali metal and alkaline earth metal compounds. It is also important to note the computational cost of the standard implementations of the various model chemistries. The ccCA computation of MP2/aug-cc-pVQZ is more expensive than the MP4/6-31G(2df,p) computation of G3X, but it is vastly less expensive than the highest level of theory used in W2 theory [CCSD(T)/aug-cc-p-V5Z+2d1f].

Comparisons of the modified G*n* and W*n* model chemistries are shown in Table 4. In the study of Sullivan and co-workers,

TABLE 3: Computed Enthalpies of Formation for G*n*, W*n*, and ccCA Procedures (in kJ mol^{-1})

molecule	ccCA-P	ccCA-S4	G2[a]	G3[b]	G3X[b]	W1[b]	W2[b]	recommended[b]
BeO	126.9	126.6	148.1	144.0	144.7	124.4	114.7	+130 ± 12
MgO	141.4	140.8	145.3	153.5	155.0	127.8	64.4	+142 ± 10
Li_2O	−160.6	−160.6	−144.0	−151.1	−151.6	−186.8	−180.9	−157 ± 5
Na_2O	−24.2	−24.6	68.5	32.1	32.4	−225.8	−18.1	−25 ± 5
LiOH	−243.9	−244.0	−238.2	−239.5	−238.8	−256.2	−250.7	−239 ± 5
NaOH	−192.7	−193.0	−194.7	−192.9	−193.0	−289.1	−187.5	−189 ± 5
$Be(OH)_2$	−634.2	−635.2	−622.3	−627.6	−623.9	−638.8	−646.8	−632 ± 7
$Mg(OH)_2$	−551.9	−552.2	−643.5	−549.7	−586.4	−582.3	−794.4	−547 ± 5

[a] Reference 7. [b] Reference 8.

TABLE 4: Computed Enthalpies of Formation for Modified G*n* and W*n* Procedures (in kJ mol^{-1})

molecule	G2[CC](dir,full)[a]	G3[CC](dir,full)[b]	W1C[c]	W2C//ACQ[d]	recommended[e]
BeO	134.4	136.8	123.5	126.6	+130 ± 12
MgO	145.1	141.1	140.0	141.7	+142 ± 10
Li_2O	−160.9	−153.9	−159.6	−159.0	−157 ± 5
Na_2O	−29.5	−28.7	−22.8	−22.7	−25 ± 5
LiOH	−245.3	−236.5	−241.8	−240.3	−239 ± 5
NaOH	−195.7	−190.0	−189.6	−188.0	−189 ± 5
$Be(OH)_2$	−634.7	−625.0	−638.6	−635.2	−632 ± 7
$Mg(OH)_2$	−549.8	−548.2	−549.3	−547.0	−547 ± 5

[a] From ref 7. All systems are computed using all-electron CCSD(T)/6-311+G(3df,2p) single point energies at MP2/6-311+G(3df,2p) geometries. [b] From ref 8. All systems are computed using all-electron CCSD(T)/G3Large single point energies at B3LYP/aug-cc-pWCVQZ geometries. [c] From ref 8. W1C is akin to the W1 method, but with a relaxed inner valence space, and cc-pWCV*XZ* basis sets are used in the CBS extrapolation. [d] From ref 8. All systems are computed with a relaxed inner valence correlation space at the CCSD(T)/aug′-cc-pWCVQZ level of theory. [e] From ref 8.

the G*n* and W*n* model chemistries must essentially be un-“black-box”-ed in order for the algorithms to predict correctly enthalpies of formation for the s-block systems under investigation.[8] For instance, the G3 method is used “without additivity assumptions” (called G3[CC](dir,full)), which is equivalent to performing expensive large basis set coupled cluster computations to determine the energy. This modified G3 model chemistry still requires a parametrized high-level correction (HLC) in order to predict accurate ΔH_f values for the test set. With the W2 method, enthalpies of formation consistent with the recommended values require very large weighted core-valence aug-cc-pWCVQZ basis sets along with all-electron CCSD(T) computations. On the contrary, the ccCA method is able to compute enthalpies for these ionic s-block compounds with accuracy similar to that of these modified methods at far less computational cost and without additional modification of the methodology employed for more covalent, p-block compounds. Since there have been no studies of larger group IA/IIA species with G*n* and W*n* methods, it is difficult to determine how reliably these composite methods will fare when computing thermochemical or spectroscopic properties of such molecules. The promising results seen here with ccCA, plus the lower computational cost compared to other model chemistries, suggest that successful computation of enthalpies of formation for larger alkali and alkaline earth metal systems will be possible.

Conclusion

A ccCA study of ionic, s-block metal compounds is presented. Such compounds have presented difficulties to previous model chemistries that perform reliably for p-block compounds. Several important conclusions emerged from this research, the most important of which are summarized here:

(a) Structures of eight group IA/IIA oxides and hydroxides obtained with B3LYP/6-31G(2df,p) showed good agreement with experimental predictions and with structures predicted at higher levels of theory.

(b) Standard G*n* methods and even W*n* methods were not designed to account for core-valence correlation of the alkali and alkaline earth metal oxides and hydroxides. When modified to account for core-valence correlation, these methods become far more computationally expensive than ccCA.

(c) For the eight molecules investigated, the two most reliable variations of the ccCA model chemistry predicted ΔH_f values within the error bars of recommended enthalpies of formation derived from computationally expensive large basis set coupled cluster computations.

(d) The ccCA method, while somewhat computationally expensive compared to G*n* methods, produces the best overall enthalpies for this test set, without any parametrizations or modifications to the standard ccCA algorithm.

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