THE JOURNAL OF
PHYSICAL
CHEMISTRY A

VOLUME 107, NUMBER 8, FEBRUARY 27, 2003

LETTERS

Theoretical Thermochemistry: Ab Initio Heat of Formation for Hydroxylamine

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Received: April 28, 2002; In Final Form: December 6, 2002

Theoretical methods are necessary to predict thermodynamic values for chemicals when sufficient experimental data or reliable estimations are not available. Hydroxylamine (HA) is an example of a highly reactive and poorly characterized compound with important industrial applications. In this work, the heat of formation for gaseous hydroxylamine is calculated, under standard conditions, using isodesmic reactions at several levels of theories, including HF, B3P86, B3LYP, MP2, MP3, MP4, CCSD(T), G2, G2MP2B3, G3B3, G3, and CBS-Q, and several basis sets, including Dunning correlation consistent and Pople-style. To gauge the computed HA values, the gaseous hydrogen peroxide heat of formation is calculated by the same methods and compared with experimental data. Also, for comparison with a traditional empirical approach, the HA heat of formation is calculated by the Benson group contribution method. On the basis of our calculations we recommend an average value of −11.4 kcal/mol for the gaseous HA heat of formation at 1 atm and 298.17 K. The mean average deviation relative to the experimental values for the methods employed is approximately 1.1 kcal/mol. These results provide guidance for selecting levels of theory and basis sets for obtaining thermochemical values, which are important for the design of safe and economical chemical processes.

Introduction

Hydroxylamine (HA), NH_2OH, has recently been involved in two major industrial incidents with disastrous consequences.[1,2] Calorimetric studies on aqueous HA indicate that it is a highly reactive compound,[3] but its properties are poorly characterized. Reliable thermochemical data for quantitative predictions of chemical reactivity and potential runaway reactions are required for designs of safe and economical industrial processes. For chemicals with validated experimental data, estimations may not be necessary, but for reactive substances with insufficient experimental data, such as hydroxylamine, estimation methods are of prime importance.

The reported experimental value for the heat of formation of gaseous HA is -12.0 ± 2.4 kcal/mol,[4] which was derived by an indirect calculation from the experimentally determined heat of formation of solid HA and the heat of sublimation.[5−7] Data from measurements of solid HA should be more reliable than data from liquid HA, because pure HA decomposes as it melts near 32 °C.[5] However, the reliability of the listed heat of formation for solid HA could not be assessed, because the experimental procedure used to determine it was not found in the original reference.[7]

Previous calculations by Sana et al.[8] yielded −11.7 kcal/mol for the heat of formation of gaseous HA using an isodesmic reaction at the MP4 level of theory. Anderson[9] determined a value of −10.6 kcal/mol by combining the calculated H_2N-OH bond energy[10] by the G1 method with the experimental heats

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10.1021/jp026027h CCC: $25.00

of formation for NH_2 and OH. Also, a heat of formation[9] of -7.9 ± 1.5 kcal/mol was derived from the appearance potential for NH_2OH[11] and heat of formation of HNO. On the basis of a statistical average of the reported theoretical and experimental values for HA, Anderson[9] recommended -9.6 ± 2.2 kcal/mol for the gaseous HA heat of formation at 1 atm and 298.17 K.

The purpose of this work is to compare theoretical methods combined with isodesmic reactions to obtain a reliable heat of formation for gaseous HA. For comparison with an estimation approach often used by industry, the HA heat of formation is calculated by the traditional Benson group contribution method. These methods together with the details of the calculations are discussed in the next section and are followed by a discussion of the results. The heat of formation values reported from this work are for gaseous species at 1 atm and 298.17 K.

Computational Methods

Benson Group Contribution Method. Benson and Buss proposed a hierarchy of additivity methods for molecular property estimations and established a theoretical framework to estimate heats of formation on the basis of “molecular groups”.[12] We employed the commercially available CHETAH[13] software, which includes the Benson group contribution method. Because the $H_2N-(O)$ and $HO-(N)$ groups were not available, the group values for $NH_2-(N)$, 11.4 kcal/mol, and $OH-(O)$, -16.27 kcal/mol, were used as substitutes for the missing ones, as recommended in the CHETAH[13] manual. This procedure yielded -4.87 kcal/mol for the gaseous HA heat of formation. However, substituting for missing group values often leads to deviations from the experimental values.

Theoretical Methods. A variety of theoretical methods, semiempirical (AM1[14]), density functional theory (B3P86[15] and B3LYP[16]), composite (G2,[17] G3,[18] G2MP2,[19] G2MP2B3,[20] G3B3,[20] and CBS-Q[21]), and ab initio (MP2,[22] MP3,[23] MP4(SDTQ),[24] CCSD,[25] CCSD(T),[26] and QCISD(T)[27]) as implemented in the Gaussian 98 suite of programs,[28] were used for geometry optimizations and frequency calculations. These calculations were performed with Dunning correlation consistent polarized valence basis sets (cc-pVDZ,[29] cc-pVTZ,[30] cc-pVQZ,[31] and cc-pV5Z,[32] where D, T, Q, and 5 refer to the number of contracted functions in each valence subshell), and Dunning correlation consistent polarized valence basis sets with diffuse functions for radial flexibility to represent electron density far from the nuclei (AUG-cc-pVDZ and AUG-cc-pVTZ). Pople-style basis sets[33,34] (6-31G, 6-31+G(d), 6-31G(d,p), 6-31+G(2df,p), 6-311G(d), 6-311+G(2df,p), 6-31+G(3df,2p), 6-311+G(3df,2p), 6-311++G(3df,2p)) including diffuse[31,35] (denoted by “+” for Pople-style) and polarization functions[36] (denoted by “d”, “p”, “f”, for angular flexibility to represent regions of high electron density among bonded atoms) were also employed. Finally, the bond additivity correction (BAC)-MP4 methodology was employed using the parameters listed by Melius and Zachariah.[37]

Errors in absolute quantities from quantum chemical calculations are often systematic. To compensate for some of the systematic errors, isodesmic reactions, which conserve the number of each type of bond in reactants and products, are used to obtain more accurate heats of formation.[38] Here, the following isodesmic reactions were employed for HA:

$$H_2 + NH_2OH \rightarrow H_2O + NH_3 \tag{1}$$

$$H_2O + NH_2OH \rightarrow H_2O_2 + NH_3 \tag{2}$$

TABLE 1: Experimental Heats of Formation (1 atm and 298.17 K)

compound	molecular formula	heat of formation (kcal/mol)
ammonia[a]	NH_3	-10.98 ± 0.084
water[a]	H_2O	-57.7978 ± 0.0096
hydrogen peroxide[b]	H_2O_2	-32.58 ± 0.05^c

[a] Reference 39. [b] Reference 40. [c] Based on the listed experimental errors.

To benchmark the computed HA values, the heat of formation for hydrogen peroxide, a similar species for which reliable experimental data are available, was calculated by the same methods and with the following isodesmic reaction:

$$H_2 + H_2O_2 \rightarrow 2H_2O \tag{3}$$

The usual procedure for calculating the heat of formation value of an unknown compound is to combine the heat of reaction obtained from an isodesmic reaction with the experimental heat of formation values for the known compounds.[38] The HA heat of formation was determined using reactions 1−2 and eqs 4−5, respectively, and H_2O_2 heat of formation was determined using reaction 3 and eq 6, using the calculated heat of reaction, $\Delta H^{Calc}{}_{Rxn}$, and the experimental heats of formation values at 1 atm and 298.17 K for ammonia,[39] water,[39] and hydrogen peroxide[40] listed in Table 1.

$$\Delta H_{f,NH_2OH} = \Delta H^{Expt}{}_{f,NH_3} + \Delta H^{Expt}{}_{f,H_2O} - \Delta H^{Expt}{}_{f,H_2} - \Delta H^{Calc}{}_{Rxn\ (1)} \tag{4}$$

$$\Delta H_{f,NH_2OH} = \Delta H^{Expt}{}_{f,NH_3} + \Delta H^{Expt}{}_{f,H_2O_2} - \Delta H^{Expt}{}_{f,H_2O} - \Delta H^{Calc}{}_{Rxn\ (2)} \tag{5}$$

$$\Delta H_{f,H_2O_2} = 2\Delta H^{Expt}{}_{f,H_2O} - \Delta H^{Expt}{}_{f,H_2} - \Delta H^{Calc}{}_{Rxn\ (3)} \tag{6}$$

The choice of isodesmic reaction is important to obtain accurate values. Although there are five single bonds on the reactant side (1 H−H, 1 O−H, 1 N−O, 2 N−H) and on the product side (3 N−H, 2 O−H) in reaction 1, the N−O bond on the reactant side is not balanced by a similar σ bond on the product side. Reaction 3 is similar to (1) in terms of bond balance with the O−O bond unbalanced on the reactant side. In reaction 2, there are six single bonds on the reactant side (3 O−H, 1 N−O, 2 N−H) and on the product side (3 N−H, 2 O−H, 1 O−O), but here the N−O bond is balanced better by the O−O bond on the product side. A better bond balance should result in a more effective cancellation of errors; therefore, reaction 2 should yield a more accurate value for $\Delta H^{Calc}{}_{rxn}$ than reaction 1 at the same level of theory. Thus we expect similar errors in the heat of formation values calculated using reactions 1 and 3, and faster convergence with increasing level of theory for reaction 2. In addition, agreement between values obtained from reactions 1 and 2 can serve as an indicator that the theory is adequate to model the system.

Discussion of Results

Values for the HA heat of formation calculated using the various levels of theory and basis sets are presented in Table 2, and computed N−O bond lengths (HA) and O−O bond lengths (hydrogen peroxide) are listed in the Supporting Information (Table SI).

The Austin Model 1 (AM1) yielded a good prediction for the hydrogen peroxide heat of formation but the heat of

TABLE 2: Summary of Calculated Heats of Formation (ΔH_f)

method	basis set	hydroxylamine heat of formation (kcal/mol) rxn 1	hydroxylamine heat of formation (kcal/mol) rxn 2	diff between rxns 1 and 2	hydrogen peroxide heat of formation (kcal/mol) rxn 3
AM1		**−32.34**	**−31.31**	**1.0**	**−33.61**
HF	**cc-pVDZ**	**−12.14**	**−12.02**	**0.1**	**−32.69**
	cc-pVTZ	−9.76	−12.48	2.7	−29.85
	cc-pVQZ	−8.83	−13.06	4.3	−28.34
	6-31G	−10.65[a]	−7.14	3.5	−35.59[a]
	6-31G(d)	−16.10	−10.69	5.4	−37.98
	6-31+G(d)	−17.47	−8.07	9.4	−33.11
	6-31G (d,p)	−11.81[a]	−12.06	0.3	−32.42[a]
	6-31+G (2df,p)	−7.65[a]	−11.71	4.1	−24.93[a]
B3P86	cc-pVDZ	−18.67	−7.79	10.9	−43.45
	cc-pVTZ	−13.99	−9.31	4.7	−37.57
	cc-pVQZ	−12.73	−10.08	2.7	−35.03
	cc-pV5Z	−12.01	−10.39	1.6	−34.20
	AUG-cc-pVDZ	**−10.62**	**−10.23**	**0.4**	**−33.00**
	AUG-cc-pVTZ	−11.83	−10.39	1.4	−34.02
	6-311G (d)	−21.70	−7.12	14.5	−47.16
	6-31+G (3df,2p)	−12.63	−10.88	1.8	−34.32
	6-311+G (3df,2p)	−12.14	−10.89	1.3	−33.83
	6-311++G (3df,2p)	−12.12	−10.89	1.2	−33.81
B3LYP	cc-pVDZ	−18.76	−5.24	13.5	−46.10
	cc-pVTZ	−14.92	−8.38	6.5	−39.12
	AUG-cc-pVDZ	−10.48	−9.26	1.2	−33.80
	AUG-cc-pVTZ	−12.18	−9.69	2.5	−35.07
	6-311+G(3df,2p)	−8.59	−6.17	2.4	−34.99
MP2	cc-pVDZ	−14.39	−9.76	4.6	−37.21
	cc-pVTZ	**−10.24**	**−11.01**	**0.8**	**−31.81**
	cc-pVQZ	−8.61	−12.09	3.5	−29.10
MP3	6-31+G(2df,p)	−8.76[a]			−28.38[a]
	cc-pVDZ	−14.44[b]	−9.82[b]	4.6	−37.20[b]
	cc-pVTZ	**−10.46**[b]	**−10.77**[b]	**0.3**	**−32.27**[b]
MP4	**6-31+G(2df,p)**	**−11.26**	**−11.89**	**0.6**	**−31.96**
MP4(SDTQ)	cc-pVDZ	−16.80[b]	−8.21[b]	8.6	−41.17[b]
CCSD(T)	cc-pVDZ	−17.05	−8.11	8.9	−41.52
	cc-pVTZ	−13.02[c]	−9.52[c]	3.5	−36.07[c]
	cc-pVQZ	**−11.56**[c]	**−10.61**[c]	**1.0**	**−33.52**[c]
QCISD(T)	cc-pVDZ	−17.08[d]	−8.12[d]	9.0	−41.54[d]
BAC-MP4	MP4//HF	−12.98	−11.09	1.9	−34.46
G2		**−11.78**	**−11.53**	**0.3**	**−32.83**
G2MP2		**−11.69**	**−11.67**	**0.0**	**−32.60**
G3		**−11.15**	**−11.28**	**0.13**	**−32.46**
G3MP2B3		**−11.88**	**−11.45**	**0.4**	**−33.01**
G3B3		**−11.51**	**−11.35**	**0.2**	**−32.74**
CBS-Q		**−12.18**	**−11.16**	**1.0**	**−33.60**
Group Additivity		- 4.87			−32.50
exptl		−12.0[e] −7.9[g]			−32.58[f]

[a] Reference 8. [b] Single point energies and thermal corrections for the enthalpies for MP3 (SDTQ) and MP4 (SDTQ) were calculated MP2/cc-pVDZ geometry. [c] Single point energies and thermal correction for the enthalpy for the CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ were calculated at CCSD(T)/cc-pVDZ geometry. [d] Single point energy and thermal correction for the enthalpy for the QCISD(T)/cc-pVTZ were calculated at CCSD(T)/cc-pVDZ geometry. [e] Based on an indirect calculation as discussed in the text (ref 4). [f] Reference 39. [g] Reference 9.

formation value obtained for HA differed significantly from the values obtained via ab initio, density functional, or the composite methods. Semiempirical methods, like AM1, perform equally well for similar compounds for which parameters are available. However, in this case, AM1 models the O−O bond in hydrogen peroxide but does not appear to work well for the N−O bond in HA.

Hartree−Fock (HF) is the lowest level ab initio theory employed in this paper for calculations. We expected HF to yield fair to good results, despite the fact that it does not include a full treatment of electron correlation, because errors are canceled by the use of isodesmic reactions. Heats of formation calculated with the Hartree−Fock model did not exhibit consistent improvement with increasing basis sets, but generally yielded more consistent results for reaction 2.

The density functional methods, although not truly ab initio, include electron correlation at only a moderate increase in computing cost, as compared to HF, by using functionals of electron density. Among the density functional methods, B3P86 yielded slightly better results for hydrogen peroxide than B3LYP for identical basis sets. However, even B3P86 with a 5Z basis set has an error of nearly 2 kcal/mol, as compared to the experimental value, for hydrogen peroxide with reaction 3. Unlike HF theory, increasing basis functions (cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z) and adding diffuse functions in the density functional methods leads toward consistent values of the heat of formation. Similar values were obtained using the 6-311+G (3df, 2p) and 6-31+G (3df, 2p) basis sets. At the density functional level of theory, there was a significant change in the calculated heat of formation from the cc-pVDZ to cc-pVTZ basis set. The magnitudes of the calculated values decreased with reaction 1 as the quality of the basis set was increased, but they increased for reaction 2. Thus, reactions 1

TABLE 3: High Level Calculated Heats of Formation

			NH_2OH heat of formation (kcal/mol)		H_2O_2 heat of formation (kcal/mol)
theory	basis set	mean average deviation	rxn 1	rxn 2	rxn 3
G2		1.2[a]	−11.78	−11.53	−32.83
G2MP2		1.6[a]	−11.69	−11.67	−32.60
G3		1.0[b]	−11.15	−11.28	−32.46
G3MP2B3		1.13[b]	−11.88	−11.45	−33.01
G3B3		0.93[b]	−11.51	−11.35	−32.74
CBS-Q		1.0[a]	−12.18	−11.16	−33.60
CCSD(T)	cc-pVQZ		−11.56	−10.61	−33.52
	Average	1.1	−11.7	−11.4	−32.9
	std dev	0.3	0.3	0.3	0.4
exptl			−12.0[c]		−32.58[d]
			−7.9[e]		

[a] Based on G2 test set of 125 molecules.[41] [b] Based on heat of formation values for 148 molecules.[20] [c] Based on an indirect calculation as discussed in the text. [d] Reference 39. [e] Reference 9.

and 2 approached the basis set limit for the heat of formation from opposite directions.

The composite theories (G2, G3, G2MP2, G3MP2B3, G3B3, and CBS-Q) are expected to yield the best results because they have been developed to model accurately thermochemical quantities for small, light-atom, main group molecules. The mean of absolute deviation (MAD) associated with heat of formation value obtained using G2 and G2MP2 theories (with the G2 test set) are 1.2 and 1.6 kcal/mol, respectively.[41] The G3 theory is a further improvement over G2 and reduces the MAD to 1.0 kcal/mol.[18] The CBS-Q accounts for errors due to basis set truncation by an extrapolation, and the MAD associated with the method is 1.0 kcal/mol.[41] The MAD associated for G3, G3MP2B3, and G3B3, based on heat of formation values for 148 different molecules, are 0.94, 1.13, and 0.93 kcal/mol, respectively.[20] All of these composite theories performed well and predicted accurate energies for hydrogen peroxide.

The MP3 (SDTQ) and MP4 (SDTQ) results were poor for cc-pVDZ, but the MP3 prediction improved with the cc-pVTZ basis set. CCSD(T)/cc-pVDZ and QCISD(T)/cc-pVDZ geometries agree well with the experimental values, but realistic energy predictions were obtained only with the cc-pVQZ basis set.

For reactions 1 and 3, as expected, the heat of formation values obtained for HA and hydrogen peroxide respectively exhibited trends in similar directions for the various levels of theory and basis sets. For the HA heat of formation values using reaction 2, there was faster convergence with the basis sets for the same level of theory. As can be seen from the heat of formation values from reaction 2, accurate values were obtained at lower levels of theory and with smaller basis sets.

Choice of Best Values. The difference between the values calculated using reactions 1 and 2 can be taken as a guide for selecting theories performing well for the system. The calculated values, in Table 2, that exhibited a difference of 1 kcal/mol or less are shown in bold. It is worth noting that these theories also predict a reasonable value for hydrogen peroxide heat of formation (within 1 kcal/mol). However, not all of these methods are reliable in other respects. Omitted from the final values to be averaged were the less reliable semiempirical AM1 predictions because the predicted values for $\Delta H_{f,\ NH2OH}$ were significantly different from the values obtained by other methods. The values obtained using theories (HF, B3P86, B3LYP) that did not demonstrate an improvement in the prediction with increasing basis set were also left out. In addition, the MP values were left out because these values did not exhibit convergence with increases in the basis set or the perturbation level.

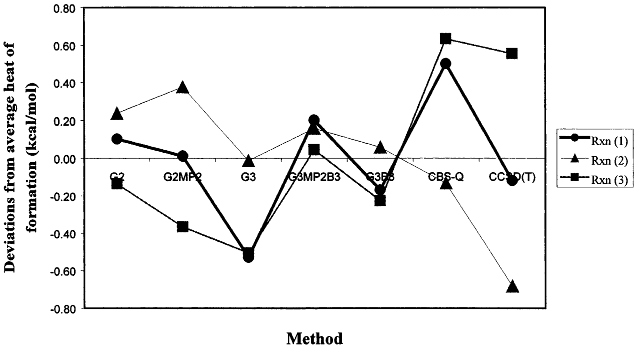

Figure 1. : Deviations from the average heat of formation values for the methods employed in Table 3.

Table 3 summarizes the seven best-predicted heat of formation values and their averages, where the calculated values using reactions 1 and 2 differed by no more than 1 kcal/mol. The average calculated heat of formation for hydrogen peroxide was −32.9 kcal/mol with a standard deviation of 0.4 kcal/mol. With reaction 1, an average value of −11.7 kcal/mol with a standard deviation of 0.3 kcal/mol was calculated. With the more balanced reaction 2, the average value was −11.4 kcal/mol with a standard deviation of 0.3 kcal/mol.

The deviations from the average heat of formation for the various methods in Table 3 are shown in Figure 1. From this pattern, it is apparent that the deviations from average for heat of formation values from reactions 1 and 3 track each other, whereas the deviations for reaction 2 do not follow the same trend. The average calculated value of ΔH_f for hydrogen peroxide is greater than the experimental value by 0.3 kcal/mol. Because reactions 1 and 3 are expected to yield similar errors, we believe that the ΔH_f value obtained using reaction 1 will differ from the true value in a similar manner and therefore recommend −11.4 kcal/mol for the ΔH_f of NH_2OH as our best estimate from both reactions 1 and 2. The mean absolute deviation (MAD) for each of the methods employed is listed in Table 3, and the average MAD value is approximately 1.1 kcal/mol. However, our HA ΔH_f values are computed from isodesmic reactions, which should yield values with smaller errors, perhaps down to twice the standard deviation of the various method. Thus the recommended ΔH_f value for HA, including our precision, judgment of methodology, and accuracy is −11.4 ± 0.6 kcal/mol. Furthurmore, the agreement and the consistency of the calculated hydrogen peroxide average value with the experimental value suggests that our calculated average value for ΔH_f of HA is more reliable than the available experimental values, which, as discussed in the Introduction, cannot be properly assessed.

Conclusions

We have investigated various computational methods to determine a reliable heat of formation for HA(g), which is a relatively unstable substance and difficult to measure accurately. Also, we have illustrated the importance of well-balanced isodesmic reactions for determining accurate heats of formation, especially at lower levels of theory. Depending on the level of theory, triple-ζ (6-311G or cc-pVTZ) or larger basis sets are necessary to predict accurate HA heat of formation values. At all levels of theory the double-ζ (6-31G or cc-pVDZ) basis set yielded poor energies, but CCSD(T) and QCISD(T) predicted accurate geometries in this basis set. On the basis of our calculations we recommend a value of -11.4 ± 0.6 (2σ) kcal/mol for the gaseous HA heat of formation at 1 atm and 298.17 K. The methods employed in obtaining the average heat of formation value have an absolute accuracy of approximately 1.1 kcal/mol, but our value obtained using isodesmic reactions is expected to have a smaller error and therefore 1.1 kcal/mol represents the maximum absolute error in the calculation. As expected, the highly parametrized composite methods (G2, G3, G2MP2, G3MP2B3, G3B3, CBS-Q) yielded the most accurate values. However, the unparametrized ab intio CCSD(T)/cc-pVQZ yielded nearly as accurate values and in some cases, depending on the accuracy needed, density functional methods, MP3, and MP4 may be adequate.

Acknowledgment. We thank the Supercomputing Facility at Texas A&M University for computer time and the Laboratory for Molecular Simulation (LMS) at Texas A&M University for software and support.

Supporting Information Available: Table summaring the bond lengths. This material is available free of charge via the Internet at http://pubs.acs.org.

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