

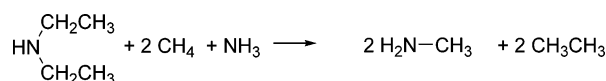
Computational Methods in Organic Thermochemistry. 2. Enthalpies and Free Energies of Formation for Functional Derivatives of Organic Hydrocarbons

Douglas Bond

Contribution from the Computer Chemie Centrum, Friedrich-Alexander-Universität, Erlangen-Nürnberg, Nögelsbach Strasse 25, 91052 Erlangen, Germany

compchemist@ichibond.org

Received June 13, 2007



Isodesmic reaction for determining ΔH_f° and ΔG_f°

Standard state enthalpies and free energies of formation for nitrogen-, oxygen-, sulfur-, fluorine-, chlorine-, and silicon-containing compounds can be computed with reasonable accuracy (usually within four and often two kJ/mol) using the G3 and G3MP2 model chemistries. In several of the families, compounds with as many as 10 carbon atoms have been computed. Larger errors are found in the free energies of these longer chain molecules which can be reduced by compensating for the presence of multiple conformers having a significant population at 298.15 K. In some instances, those substances showing large deviations are found to have experimental energies that may be erroneous.

Introduction

Enthalpies and entropies of formation are readily obtained from the NIST Webbook (WB)¹ and the Computational Chemistry Comparison and Benchmark Database (CC).² One or both of these have values for most of the alkanes and alkenes having seven or fewer carbon atoms; however, complete data for compounds having functional groups is available only for those having up to four carbon atoms. Enthalpy values may be reported for larger molecules that are structurally simple, but entropies from which the free energies are computed are often missing. Thermodynamic data from group additivities, developed by the Benson³ and Sussex⁴ groups, is an attempt to fill in the gaps in the data available from thermochemical measurements. Tabulations of estimates for the alcohols,⁵ thiols,⁶ and

chlorides⁷ based on the Benson method have appeared, and a comprehensive work covering most of the functional groups has been published by Damalski and Hearing.⁸ Nevertheless, difficulties remain because reference data for some of the functional groups are still debated (fluorine compounds or the diazenes are good examples) and interactions between functional groups in polyfunctional molecules are not well documented. The most flexible approach to this problem, although not necessarily the cheapest, is computations that evaluate a molecule from first principles.⁹

In a recent paper, we reported an evaluation of several high-level model chemistries as means of determining the enthalpies and free energies of formation for aliphatic hydrocarbon molecules.¹⁰ We were not the first off the block as numerous papers have been published over the past 15 years exploring this possibility, and the methodology has been reviewed.¹¹ Our work was the first comprehensive review of computational methodologies used to compute free energies. In that work, we

(1) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook*; Linstrom, P. J., Mallard, W. G., Eds.; NIST Standard Reference Database No. 69; National Institute of Standards and Technology, Gaithersburg, MD, June 2005 (<http://webbook.nist.gov>).

(2) *NIST Computational Chemistry Comparison and Benchmark Database*; Johnson, R. D., III, Ed.; NIST Standard Reference Database No. 101, Release 11, May 2005 (<http://srdata.nist.gov/cccbdb>).

(3) (a) Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419. (b) Benson, S. W. *Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*, 2nd ed.; Wiley: New York, 1976.

(4) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

(5) Alberty, R. A.; Chung, M. B.; Flood, T. M. *J. Phys. Chem. Ref. Data* **1987**, *16*, 391.

(6) Alberty, R. A.; Burmenko, E.; Kang, T. H.; Chung, M. B. *J. Phys. Chem. Ref. Data* **1987**, *16*, 193.

(7) Alberty, R. A.; Chung, M. B. *J. Phys. Chem. Ref. Data* **1990**, *19*, 321.

(8) Domalski, E. S.; Hearing, E. D. *J. Phys. Chem. Ref. Data* **1993**, *22*, 805.

(9) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

(10) Bond, D. *J. Org. Chem.* **2007**, *72*, 5555.

(11) Curtiss, L. A.; Redfern, P. C.; Frurip, D. J. *Rev. Comput. Chem.* **2000**, *15*, 147.

found that the most reliable results and flexible methods were obtained with the G3 or G3MP2 (alternatively the G3B3 or G3MP2B3) model chemistries. Enthalpies are customarily within 4 kJ/mol of experiment and usually within 2. Free energies are often quite close to experiment, but diverge as the molecules become larger, typically being higher than the experimental result. This trend is a result of the importance of higher energy conformers which have significant populations at standard conditions. To compensate for this, we determined a set of corrections based upon the number of bonds that can be rotated to afford additional conformations. When the computational results are adjusted by these corrections, they agreed with experiment within 2 kJ in most cases.

The problem of correcting for errors in the entropy has been looked at by several groups. Vansteenkiste et al.¹² examined a one-dimensional hindered rotor approach and found it to be effective for organic compounds having a sulfur or oxygen atom. East et al.¹³ were able to achieve entropy accuracies within 1 J/mol K by explicitly treating internal rotation and considering rotor–rotor coupling. An alternate approach, reported by Guthrie,¹⁴ ignored problems arising from the frequencies and focused on the errors arising from the omission of the effects of the entropy of mixing. His approach differs from ours in that the corrections are applied to the computed entropy rather than the free energy. Because the free energies are available directly from the output and the math is easier, we prefer to apply the corrections at the end stage. In this paper, we extend these results to compounds having one or more nitrogen, oxygen, sulfur, halogen, and silicon atoms.

Methods

We have made extensive use of the CCCBDB library of computational results.² To augment what is available, we have employed the Gaussian 98¹⁵ suite of programs and more recently, Gaussian 03.¹⁶ All compounds were calculated with the G3MP2 model chemistry. Those having seven carbon atoms or fewer were also computed using the G3 model. A few larger compounds having C_s or higher symmetry were also computed at this higher level. As this work was nearing completion, Curtiss et al. published the parameters for Gaussian 4, a new model chemistry.¹⁷

The absolute energies were converted into formation energies using isodesmic bond separation reactions method which we explained in our initial report on the hydrocarbons. Exceptions to this will be noted in the discussion. The tables show first the enthalpies, then the free energies. The last column shows the G3 computed free energy (G3MP2 for larger molecules) adjusted by our corrections.

To determine these corrections, we subtract 1.2 kJ/mol for each bond whose rotation affords a new conformation. In determining the number of rotatable bonds, we counted all carbon–carbon bonds whose rotation affords different conformers except those (a) adjacent to quaternary centers and (b)

TABLE 1. Mean Absolute Deviations^a for Aliphatic Organonitrogen Determined by G3 and G3MP2 Model Chemistries Using Isodesmic Bond Separation Reactions

molecule	enthalpies of formation		free energies of formation	
	G3	G3MP2	G3	G3MP2
primary amines	2.3	2.2	4.2	4.4
secondary amines	2.3	2.0	6.2	6.2
tertiary amines	5.7	5.8	11.4	11.1
hydrazines	5.9	4.9		
nitriles	4.4	6.0	1.2	2.0
amides	2.2	3.5	9.1	5.4

^a kJ/mol.

between tertiary centers that are separated by one or two bonds.¹⁸ In our first paper, we reported that the bond adjacent to a carbon–carbon double bond made a larger contribution, 2.5 kJ/mol, to the correction. In this work, we have found that this same value works equally well with the alcohol and chlorine functional groups. Sulfur uses a smaller value of 0.5 kJ/mol, and there is too little data for fluorine compounds to determine if the corrections are valid in these cases. These values were determined by explicitly computing the energies of all conformations derived by rotation of the bonds adjacent to the functional group for the two or three simplest homologues of a family of compounds. We then used this as a trial value in our spreadsheets to find that value which would give the lowest mean absolute deviation for the full spectrum of compounds in our database. We noted earlier that no compensation for bonds to quaternary carbon atoms was allowed. Quaternary is defined for this work as any carbon atom having no bond to hydrogen. Thus, the central carbon in *tert*-butyl alcohol or *tert*-butyl chloride is considered quaternary by this definition and the corresponding correction is not applied. Other, more specific, exceptions will be discussed at the appropriate point in the discussion section which follows.

Experimental values are taken primarily from refs 1 and 2 and to a lesser extent from ref 8. These were cross checked against a compilation of experimental enthalpies from the literature that have been critically reviewed by Cioslowski and co workers.¹⁹ The concept that the methylene group ($-\text{CH}_2-$) has a constant value (20.6 kJ/mol) in a hydrocarbon chain appears to be valid in a variety of functionalized homologous series. When we encounter discrepancies, the difference between the enthalpy or free energy value in question and those preceding or following in the series is compared to this methylene constant. This analysis is applied to both the experimental and computed results to determine which is more likely to be in error. In essence, we have used Benson's group equivalents as a cross-check.³

Results and Discussion

Nitrogen. The mean absolute deviations of the nitrogen compounds are shown in Table 1. It is clear that the enthalpies for the primary and secondary amines along with the amides fall within our ideal range. The others do not. For the free energies, only the nitriles have this level of accuracy. The overall accuracy of the primary amines can be brought into the ideal

(12) Vansteenkiste, O.; Verstraelen, T.; Van Speybroeck, V.; Waroquier, M. *Chem. Phys.* **2006**, *328*, 251.

(13) East, A. L. L.; Radom, L. *J. Chem. Phys.* **1997**, *106*, 6655.

(14) Guthrie, J. P. *J. Phys. Chem. A* **2001**, *105*, 8495.

(15) Gaussian 98, Revision A.11.3, M. J. Frisch, et al. Complete citation is found in the Supporting Information.

(16) Gaussian 03, Revision D.02; M. J. Frisch, et al. Complete citation is found in the Supporting Information.

(17) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **2007**, *126*, 084108.

(18) For example, 2,2-dimethylhexane has two rotatable bonds and 2,4-dimethylhexane has one.

(19) Cioslowski, J.; Schimeczek, M.; Liu, G.; Stoyanov, V. *J. Chem. Phys.* **2000**, *113*, 9377.

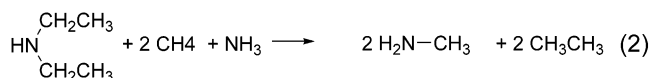
TABLE 2. Comparison of the Enthalpies and Free Energies^a for Selected Secondary and Tertiary Amines Calculated Using the G3MP2 Model Chemistry Using Isodesmic and Semi-homodesmotic Bond Separation Reactions

molecule	G3MP2 enthalpy of formation			G3MP2 free energies of formation		
	literature	isodesmic	homodesmotic	literature	isodesmic	homodesmotic
secondary amines						
diethylamine	-72.5	-76.7	-76.5	76.8	70.8	77.6
dipropylamine	-116.5	-118.0	-117.8	90.0	90.9	97.6
dibutylamine	-156.6	-160.0	-159.8	107.8	110.5	117.2
azacyclopropane	126.5	125.8	126.2	185.8	179.4	186.4
azacyclopentane	-3.5	-4.9	-5.7	119.6	113.9	119.6
azacyclohexane	-47.2	-50.7	-51.8		105.9	111.4
tertiary amines						
triethylamine	-92.8	-98.9	-93.5	122.0	111.2	122.8
tripropylamine	-157.1	-162.8	-157.4	143.1	138.9	150.5

^a kJ/mol.

range by correcting for the presence of multiple conformers. The values of the secondary and tertiary amines cannot be improved in this way because the computed free energies are already lower than those derived by experiment.

The deviations above were computed using isodesmic bond separation reactions as illustrated for ethyl and diethyl amine in eqs 1 and 2, respectively. These have methyl amine and ethane as the end products.



The deviations for the secondary and tertiary amines shown in Table 1 can be improved by using a semi-homodesmotic process for the amines. We retain the isodesmic process for the carbon and hydrogen bonds, but use dimethyl and trimethyl amine as the nitrogen end-products. This will remove the necessity of having ammonia as one of the reactants and affords molecules having the same number of secondary or tertiary nitrogen atoms on both sides of the reaction arrow. Examples using diethyl- and triethylamine are shown in eqs 3 and 4, respectively.

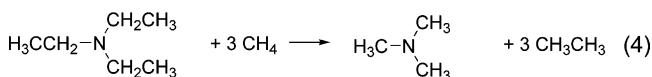
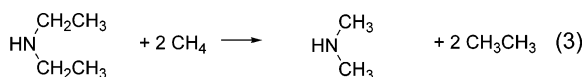


Table 2 compares both enthalpies and free energies for the secondary and tertiary amines calculated using the isodesmic and semi-homodesmotic processes described above.

It is clear that there is little, if any, difference between the two methods for the secondary amine enthalpies which are very close to the experimental values. For tertiary amines, the method does make a difference. Enthalpies computed using the isodesmic reactions differ significantly from experiment while those calculated with homodesmotic equations are much closer. The isodesmic method is unable to compute accurate free energies for either secondary or tertiary amines. Better results are obtained with the semi-homodesmotic reactions and as we will show in the discussion below, most of the larger differences in the latter can be reduced by compensating for rotation around the carbon-carbon bonds. Several other groups have reported using homodesmotic reactions for these types of compounds.

Boatz and Gordon²⁰ examined secondary heterocyclic rings using smaller basis sets than we have employed, Nielsen²¹ examined the azacyclopropanes at higher basis sets, da Silva et al.²² studied the isomeric methylazacyclohexanes using homodesmotic reactions for the secondary amines. However, for the tertiary 1-methylpyridine an isodesmic equation was employed. For the low molecular weight 1-substituted primary amines, Bodi et al. used an isodesmic equation in which an alcohol was the exchange partner.²³

Complete results for all nitrogen-containing compounds which we have examined are shown in Table 3 and include four groups of compounds: amines, hydrazines, nitriles, and amides.

The enthalpies of the primary amines fall into our ideal range in all cases except for cyclopropylamine. Indeed, with this value excluded from the average, the mean absolute deviation drops to 2 kJ/mol. Bodi et al.²³ used threshold photoelectron photoion coincidence spectroscopy to examine the low molecular weight primary amines and compared the results with ab initio calculations. Based on their results, they suggested revised enthalpies of formation for (a) ethanamine, -50.1 kJ/mol, and (b) 1-propanamine, -70.8 kJ/mol. Both of these are somewhat closer to our computed results. Two compounds, ethanamine and 2-methyl-2-propanamine, have deviations that are larger than 2 kJ/mol. The deviation of the latter is a prototype for subsequent families of compounds that we will examine in which a heteroatom bonded to a tertiary carbon often show larger deviations.

The values for dimethyl- and trimethylamine deviate significantly from experiment. Since they are the basis of the homodesmotic equations 3 and 4, they have been calculated by an isodesmic equation and are excluded from the mean deviation for each group. The enthalpies of the remaining compounds are quite good. Diethylamine lies just outside the ideal range as does the G3 enthalpy for azacyclohexane. The cyclic secondary amines have been the subject of several computational studies. Recent work done at high levels of theory includes the azacyclopropane work by Nielsen²¹ and the computation of the substituted azacyclohexanes by da Silva et al.²² An examination of all four of the heterocyclic amines reported here has been published by Vayner and Ball.²⁴ They used several lower level

(20) Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* **1989**, *93*, 3025.(21) Nielsen, I. M. B. *J. Phys. Chem. A* **1998**, *102*, 3193.(22) da Silva, M. A. V. R.; Cabral, J. I. T. A.; Gomes, P.; Gomes, J. R. *B. J. Org. Chem.* **2006**, *71*, 3677.(23) Bodi, A.; Kercher, J. P.; Bond, C.; Meteesatien, P.; Sztaray, B.; Baer, T. *J. Phys. Chem. A* **2006**, *110*, 13425.(24) Vayner, E.; Ball, D. W. *Theochem* **2000**, *496*, 175.

TABLE 3. Experimental Enthalpies and Free Energies of Formation^a and Deviations for Aliphatic Organonitrogen Determined by G3 and G3MP2 Model Chemistries Using Semi-homodesmotic Equations

molecule	source ^b	enthalpies of formation			free energies of formation			corrected ^c
		literature	G3	G3MP2	literature	G3	G3MP2	
primary amines								
ethanamine	CC	-47.5	-51.1	-51.1	36.2	35.1	35.2	33.9
1-propanamine	CC	-70.1	-72.1	-71.9	41.9	44.8	45.1	42.4
1-butanamine	CC	-92.0 ^d	-93.0	-92.6	49.4	54.7	55.1	51.1
1-pentanamine	GA	-113.2	-114.1	-113.8	57.0	64.3	64.7	59.5 ^e
1-hexanamine	GA	-133.8	-135.8	-135.2	65.5	73.4	74.0	67.4
2-propanamine	CC	-83.7	-87.4	-87.1	32.2	31.0	31.3	29.8
2-butanamine	DH	-104.9 ^f	-107.6	-107.2	40.1	41.8	42.2	39.4
1-amino-2-methylpropane	CC	-98.6	-100.5	-100.3		48.8	49.0	46.4
2-methyl-2-propanamine	CC	-120.7	-124.4	-123.7	35.8	27.1	27.8	
cyclopropanamine	CC	77.3	83.9	85.0	166.9	168.4	169.5	
cyclobutanamine	CC	41.0	40.2	41.3		159.5	160.6	
cyclopentanamine	DH	-54.9	-55.7	-54.4		94.4	95.7	
cyclohexanamine	DH	-104.9	-107.7	-106.4		81.2	82.5	
1,2-diaminoethane	DH	-17.6	-16.7	-16.4	112.2	108.0	108.3	
1,2-diaminopropane	DH	-53.6	-51.6	-51.0		105.2	105.8	
1,2-diaminobutane	DH	-74.0	-72.1	-71.3		115.6	116.4	
secondary amines								
dimethylamine	CC	-18.6	-18.6	-18.8	73.7	67.2	67.0	
ethylmethylamine			-47.7	-47.6		75.5	75.6	74.3
propylmethylamine	CC		-67.7	-67.4		86.6	86.8	84.2
isopropylmethyl amine			-80.7	-80.4		74.3	74.6	74.3
diethylamine	DH	-72.5	-76.8	-76.5	76.8	77.3	77.6	74.9
dipropylamine	WB	-116.5	-118.5	-117.8	90.0	97.0	97.6	92.2
dibutylamine	DH	-156.6		-159.8	107.8		117.2	110.0 ^g
azacyclopropane	DH	126.5	126.2	126.0	185.8	186.4	186.2	
azacyclobutane			97.5	98.3		191.1	191.9	
azacyclopentane	CC	-3.5	-5.7	-4.7	119.6	119.6	120.6	
azacyclohexane	CC	-47.2	-51.8	-50.5		111.4	112.7	
tertiary amines								
trimethylamine	DH	-23.7	-28.9	-29.1	103.9	91.8	92.3	
ethyldimethylamine			-48.7	-49.0		106.7	105.6	105.5
triethylamine	DH	-92.8	-93.8	-93.5	122.0	123.2	122.8	119.6
tripropylamine	GA	-157.1		-157.4	143.1		150.5	143.3 ^g
hydrazines								
methylhydrazine	DH	94.6	102.8	102.0		193.6	192.8	
1,1-dimethylhydrazine	DH	84.0	86.3	85.3		210.1	209.1	
1,2-dimethylhydrazine	DH	92.0	99.1	98.1		220.7	219.7	
nitriles								
ethanenitrile	CC/WB	74.0 ^h	75.3	76.4	96.6	90.2	91.3	
propanenitrile	DH	51.5	56.3	57.7	101.8	101.6	103.1	
butanenitrile	CC	33.5	34.0	35.6	112.4	110.2	111.8	109.0
pentanenitrile	WA/GA	11.1 ⁱ	12.6	14.3	119.6	119.6	121.3	117.2
propenenitrile	DH	183.7	187.8	190.0	198.4	198.0	200.2	
amides								
methanamide	CC	-186.0	-190.4			-150.8	-147.9	-150.8
ethanamide	CC	-238.5	-236.2	-232.5	-158.5	-167.6	-163.9	-167.6
propanamide	CC	-258.9	-258.5	-254.5		-158.2	-154.1	-158.2
2-methylpropanamide		-282.6	-286.2	-281.3		-155.8	-151.0	-155.8
butanamide	CC	-279.2	-279.5	-275.2		-148.4	-144.2	-148.4
overall			2.9	3.0		3.2	3.7	1.8
primary amines			2.3	2.2		4.2	4.4	1.7
secondary amines			2.7	2.3		2.0	4.3	2.1
tertiary amines			1.0	0.5		1.2	4.1	1.3
hydrazines			5.9	4.9				
nitriles			4.4	6.0		1.2	2.0	
amides			2.2	3.5		9.1	5.4	

^a kJ/mol. ^b WB, ref 1; CC, ref 2; DH, literature cited in ref 8; GA, values determined by group additivity method in ref 8. ^c A constant value of 1.2 kJ/mol per rotatable carbon-carbon and carbon-nitrogen bond is subtracted from the G3 computed energy. ^d Reference 1 gives a value of -95. kJ/mol for the enthalpy. ^e Explicit calculation of all conformers gives a value of 59.6 kJ/mol. ^f Reference 1 gives a value of -106. kJ/mol for the enthalpy. ^g Corrected values based on the G3MP2 energy. ^h The enthalpy is from reference 1; the entropy from ref 2. Reference 2 gives a value of 64.4 kJ/mol for the enthalpy. ⁱ The enthalpy is from ref 1; the entropy is from group additivity values found in ref 8.

ab initio basis sets as well as a spectrum of density functional methods to obtain enthalpies of formation that have larger deviations than those shown in Table 3.

The mean deviation for the free energies of the primary amines is somewhat larger than that for the enthalpies, falling just below the cutoff for the ideal range. Examining the

homologous series beginning with ethanamine, we find that the errors are larger than those of the enthalpies and become larger as the chain length increases. We have corrected for multiple conformations by subtracting the 1.2 kJ/mol per rotatable bond. This includes the carbon-nitrogen bond as well. Thus ethanamine would have one rotatable bond and 1-propanamine, two, etc.

Only ethanamine is not improved by correction, but we noted earlier that other work has suggested a value of -50.1 kJ/mol for the enthalpy. If this value is correct, then the corresponding free energy is 33.6 kJ/mol, which is virtually identical to our result. The one diamine for which we have entropy data is not improved by correction either. After correction, all of the secondary and tertiary amines have free energies that fall within our ideal range.

We present data for three substituted hydrazines. As can be noted from Table 1, the mean deviation is outside our ideal range but still acceptable. The difficulty with these values may stem from the experimental value of hydrazine for which reference 1 lists three different values spanning a range of 100 kJ/mol! We have clearly used the value which gives the best results and the closeness of our computations for the other three compounds suggests that the midrange value for hydrazine that we have employed is probably closest to the true value. No comparison data for the free energies is available for these compounds. There are no reports in the literature of computational determination of the enthalpies of these compounds, although Nielsen²¹ and Ma et al.²⁵ have used one or more of these as reference compounds to determine the enthalpies of their homologs.

Experimental data for very few nitriles are available. Only the two three-carbon nitriles show significant deviations from experiment, and these are within our acceptable range. In the case of propanenitrile, group additivity principles could be used argue for a higher experimental value that would match our value more closely. The free energies for these compounds are quite good. The amide enthalpies are also in reasonable agreement with experiment. Unfortunately, only one of these compounds has an experimental free energy and the agreement here is not good. Politzer et al.²⁶ has reported a density functional enthalpy for ethanamide which is nearly 10 kJ/mol higher than our value.

Oxygen. The thermodynamic properties of oxygen-containing organic compounds can be computed with reasonable accuracy, although they are slightly less accurate than those of the hydrocarbons. The results are found in Table 4. Only the G3MP2 free energies do not fall into the ideal range. We frequently observe that the mean deviation for G3MP2 free energies is larger than that resulting from G3 calculations, not because the former is an inherently less accurate, but because we are able to compute much larger molecules. Since the errors before correction are a function of the size of the molecule, G3MP2 will appear less accurate than the former method.

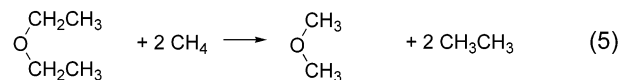
The mean deviation of the alcohol enthalpies is smaller than the overall average, but the free energy mean deviation is larger. Examining the homologous series of compounds derived from ethanol, the computed enthalpies of most of the higher molecular weight members differ from experiment by $5-8$ kJ/mol. Our results for the series up to 1-decanol differ from each other by approximately the Benson methylene equivalent. In these cases, our computed results are in better agreement with group additivity enthalpies; all within four kJ/mol. It would appear that computation is often better at reproducing group additivity than is experiment and the correspondence gives credence to both as a reliable source of thermodynamic data. In those

instances where experiment and values from ref 5 differ by more than 2 kJ/mol, we have given the group additivity value in the footnotes to the tables. Our computed values for two of the isomeric pentanols also differ from experiment by more than 4 kJ/mol and in each case, the group additivity value comes closer to the computed result than to experiment.

The calculated enthalpies of the three diols and one unsaturated alcohol for which we have data also agree quite well with experiment. There is no experimental value for cyclopropanol; however, our result compares favorably with that of Rogers, et al.²⁷ which was determined using the G2 method. Cyclobutanol and cyclopentanol are within our ideal range for both the G3 and G3MP2 models; however, the value for cyclohexanol is significantly lower than the experimental value and we have chosen the value (of two) which best approximates our results. The G3 enthalpy is outside our acceptable range, and further work is required on this system.

The mean absolute deviation for the alcohol free energies is larger than our ideal until the corrections are applied. We subtract a constant value of 2.5 kJ/mol for the oxygen and 1.2 kJ for each rotatable carbon-carbon bond. As noted in the introduction, no correction is taken for tertiary oxygen atoms. With the corrections most free energies are within 2 kJ/mol of experiment. The only major deviation, 1-heptanol, is off by more than five kJ/mol. It is intriguing that this compound was the only member of its homologous series to have an enthalpy that was close to experiment; however, the free energy derived from group additivity entropies³ is very close to our determination.

We have also used semi-homodesmotic equations, illustrated in eq 5 for diethyl ether, to calculate the thermodynamic parameters for the ethers, although the improvement is modest compared to that seen for the amines.



Our enthalpies for the ethers, both cyclic and acyclic, have mean deviations that are comparable to those recorded for the alcohols and lie well within our ideal range. A few compounds are outside the ideal range in either the G3 or G3MP2 computed value, but none of these differ from experiment by more than 5 kJ/mol. Looking at the homologous series derived from methoxyethane, we see that both experimental and computed values increase by the same incremental values. That we are consistently lower may be due to either a systematic error in the computations or the experimental determination. Our results are within 1 kJ/mol of those published by Sumathi and Green²⁸ using the CBS-Q model with one exception. They included the spin-orbit and bond additivity corrections recommended by Peterson²⁹ and used the atomization method to convert the absolute energies into enthalpies of formation. The exception is methyl *tert*-butyl ether for which they obtained a value within 2 kJ/mol of experiment.

With two exceptions, the cycloethers are also computed accurately: 1,3-dioxolane and trioxane. Removal of these from the G3 mean deviation calculation drops the mean deviation to

(27) Rogers, D. W.; McLafferty, F. J.; Podosenin, A. V. *J. Org. Chem.* **1998**, *63*, 7319.

(28) Sumathi, R.; Green, W. H., Jr. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3402.

(29) Petersson, G. A.; Malick, D. K.; Wilson, W. G.; Ochterski, J. W.; Montgomery, J. A., Jr.; Frisch, M. J. *J. Chem. Phys.* **1998**, *109*, 10570.

(25) Ma, B.; Lii, J-H, Chen, K.; Allinger, N. L. *J. Phys. Chem.* **1996**, *100*, 11297.

(26) Politzer, P.; Murray, J. S.; Grice, M. E.; Desalvo, M.; Miller, E. *Mol. Phys.* **1997**, *91*, 923.

TABLE 4. Experimental Enthalpies and Free Energies of Formation^a and Deviations for Aliphatic Compounds Containing One or More Oxygen Atoms and Determined by G3 and G3MP2 Model Chemistries Using the Bond Separation Method

molecule	source ^b	enthalpies of formation			free energies of formation			corrected ^c
		literature	G3	G3MP2	literature	G3	G3MP2	
alcohols								
ethanol	CC	-235.0	-235.1	-234.8	-167.8	-165.6	-165.3	-168.1
1-propanol	CC	-255.2	-256.0	-255.5	-159.9	-155.5	-155.0	-159.2
1-butanol	WB	-275.3	-277.2	-276.6	-151.0	-145.9	-145.2	-150.8
1-pentanol	WB	-295.6	-298.6	-297.9	-142.4	-136.6	-135.8	-142.7 ^d
1-hexanol	WB	-314.7 ^e	-320.1	-319.1	-132.3	-126.6	-126.3	-133.9
1-heptanol	WB	-339.7 ^f		-340.4	-130.4		-116.7	-125.2 ^g
1-octanol	WB	-355.6 ^h		-361.6	-115.7		-107.2	-116.9 ^g
1-nonanol	WB	-375.5		-382.9	-106.5		-97.8	-108.7 ^g
1-decanol	WB	-396.6		-403.8	-98.6		-88.0	-100.1 ^g
2-propanol	CC	-272.7	-274.5	-272.5	-173.4	-173.0	-171.2	-175.5
2-butanol	WB	-293.0	-296.0	-295.0	-166.8	-163.5	-162.5	-167.2
2-pentanol	WB	-314.6	-316.5	-315.2	-158.6	-153.3	-152.0	-158.2
3-pentanol	WB	-314.7	-316.9	-315.5	-155.8	-153.4	-152.0	-155.9
2-methyl-1-propanol	WB	-283.8	-285.5	-284.9	-156.0	-153.1	-152.5	-155.6
2-methyl-1-butanol	WB	-302.0	-304.3	-303.5		-141.0	-140.2	-144.7
2-methyl-2-propanol	CC	-312.4	-315.7	-312.3	-177.6	-181.3	-178.1	
2-methyl-2-butanol	DH	-329.4 ⁱ	-334.8	-333.1	-165.9	-168.9	-167.2	-168.9
3-methyl-1-butanol	WB	-301.3	-304.4	-303.6		-141.2	-140.4	-144.9
3-methyl-2-butanol	WB	-316.4 ^j	-321.0	-319.8	-159.4	-156.5	-155.3	-159.0
2,2-dimethyl-1-propanol		-318.4	-320.5	-319.4		-154.6	-154.7	
1,2-ethanediol	DH	-387.5	-389.4	-388.3	-302.5	-296.4	-295.3	-301.4
1,2-propanediol	CC	-429.8	-427.0	-425.3		-302.1	-300.5	-307.1
1,3-propanediol	WB	-408.4	-413.4	-411.8		-287.9	-286.2	-292.9
2-propen-1-ol	DH	-124.5	-126.9	-125.9	-63.6	-62.1	-61.2	-67.1
cyclopropanol			-101.4	-100.0		-32.4	-31.0	
cyclobutanol	CC	-144.8	-146.1	-144.9		-43.3	-42.1	
cyclopentanol	CC	-242.6	-241.2	-239.4		-108.1	-106.4	
cyclohexanol	WB	-286.2	-294.7	-292.7	-117.2	-122.6	-120.6	
ethers								
methoxyethane	CC	-216.5	-219.0	-218.6	-117.2	-117.0	-116.7	-118.4
1-methoxypropane	WB	-238.0	-240.0	-238.7	-110.8	-107.0	-106.1	-109.4
1-methoxybutane	WB	-258.1	-261.3	-260.6	-101.6	-97.5	-96.8	-101.1
2-methoxypropane	WB	-252.0	-253.3	-252.5	-121.7	-120.6	-119.8	
2-methoxy-2-methylpropane	DH	-283.5	-287.7	-286.3	-115.9	-123.5	-122.1	
diethyl ether	CC	-250.8	-253.7	-252.9	-120.8	-119.3	-118.5	-121.7
1-ethoxypropane	CC	-272.2	-274.1	-273.2	-115.1	-110.7	-109.8	-114.3
dipropyl ether	DH	-293.1	-296.2	-295.0	-105.6	-101.3	-100.1	-113.7
diisopropyl ether	DH	-319.4	-324.1	-322.1	-122.3	-127.2	-125.2	
isopropyl <i>tert</i> -butyl ether	DH	-357.7		-355.2	-128.2		-124.2	
dibutyl ether	DH	-332.9		-336.3	-87.3		-79.9	-87.1
di <i>sec</i> -butyl ether	DH	-360.7		-365.0	-103.8		-105.5	-107.9
dimethoxymethane	CC	-348.2	-353.3	-352.3		-225.8	-224.8	
cycloethers								
oxirane	CC	-52.6	-52.2	-51.9	-13.2	-13.0	-12.8	
propylene oxide	CC	-93.7	-94.6	-93.8	-25.0	-24.6	-23.7	
oxetane	CC	-80.5	-79.8	-78.7	-8.9	-7.6	-8.2	
tetrahydrofuran	CC	-184.2	-183.0	-181.6	-81.1	-78.8	-77.4	
tetrahydropyran	CC	-233.8	-224.2	-222.7		-82.1	-80.7	
3,3-dimethyloxetane	CC	-148.2	-148.9	-147.2		-15.4	-13.5	
1,3-dioxolane	WB	-301.7	-297.0	-295.6	-211.1	-203.6	-202.2	
2-methyl-1,3-dioxolane	CC	-350.8	-350.8	-348.4		-221.9	-219.5	
1,3-dioxane	WB	-338.4	-342.3	-340.4		-207.1	-205.3	
1,4-dioxane	WB	-315.3	-318.8	-317.0	-180.9	-182.1	-180.3	
trioxane	CC	-465.8	-471.9	-470.0	-337.0	-340.9	-339.0	
peroxides								
methyl hydroperoxide	CC	-131.0	-131.0	-131.4		-38.1	-38.5	
ethyl hydroperoxide	WB	-210.0	-165.0	-165.0		-40.6	-40.6	
propyl hydroperoxide	WB	-250.0	-185.5	-185.2		-30.4	-30.2	
butyl hydroperoxide	WB		-206.5	-206.1		-20.7	-20.2	
isopropyl hydroperoxide	CC	-197.1	-204.6	-203.8		-48.3	-47.5	
<i>tert</i> -butyl hydroperoxide	DH	-245.9	-245.4	-243.9		-55.6	-54.1	
dimethyl peroxide	DH	-125.9	-127.3	-128.4		-4.4	-5.5	
diethyl peroxide	DH	-192.8	-195.2	-195.3		-7.7	-7.8	

Table 4 (Continued)

molecule	source ^b	enthalpies of formation			free energies of formation			corrected ^c
		literature	G3	G3MP2	literature	G3	G3MP2	
aldehydes								
ethanal	CC ^k	-170.7	-164.1	-163.0	-137.5	-131.1	-130.0	
propanal	CC	-186.0	-186.4	-185.1	-124.2	-121.9	-120.5	-123.1
butanal	CC	-206.6	-206.9	-205.4	-115.9	-111.5	-110.0	-113.9
pentanal	GA	-228.5	-228.4	-226.7	-108.8	-102.2	-100.6	-105.8 ^l
hexanal			-249.8	248.1		-92.8	-91.9	-97.6
heptanal	WB	-264.0		-269.3	-86.4		-81.6	-86.6
octanal	GA	-291.6		-290.6	-85.1		-72.1	-78.1
nonanal	GA	-312.3		-311.8	-76.7		-62.6	-69.6
2-methylpropanal	CC	-215.8	-210.9	-209.1		-117.2	-115.4	-117.2
2-methylbutanal			-233.0	-231.1		-108.5	-106.6	-108.5
3-methylbutanal			-235.7	-234.1		-109.7	-108.1	-109.7
glyoxal	CC	-212.0	-212.1	-209.8	-189.7	-189.7	-187.4	
ketones								
propanone	CC	-217.1	-215.0	-213.0	-152.6	-152.9	-150.9	
2-butanone	CC	-238.6	-237.5	-235.3	-146.6	-146.2	-143.9	-146.2
2-pentanone	DH	-259.1	-258.2	-255.8	-137.3	-136.3	-133.8	-137.5 ^m
2-nonanone	WB	-343.4		-341.0	-105.1		-96.1	-101.1
3-pentanone	DH	-258.0	-260.1	-257.5	-134.4	-137.2	-132.9	-137.2
3-methyl-2-butanone	CC	-262.6	-259.1	-259.7		-133.0	-134.1	-133.0
2,3-butanedione	CC	-326.8	-327.4	-322.8		-247.3	-242.7	
cyclopropanone	CC	16.0	20.6	23.1	51.1	53.1	55.6	
cyclobutanone	WB ⁿ	-91.6	-88.0	-85.3		-25.9	-23.2	
cyclopentanone	CC	-192.1	-194.2	-190.9	-90.7	-94.0	-90.7	
cyclohexanone	DH	-222.7	-229.5	-226.1	-83.2	-94.8	-91.4	
carboxylic acid								
methanoic acid	CC	-378.8	-377.4	-375.9	-351.2	-350.2	-348.7	
ethanoic acid	CC	-432.3	-430.7	-427.9	-374.3	-374.5	-371.7	
propanoic acid	DH	-458.7	-453.2	-450.0		-365.5	-362.3	
2-methylpropanoic acid			-479.2	-475.5		-359.6	-355.9	
butanoic acid	DH	-475.8	-474.6	-471.2		-354.9	-351.5	
oxalic acid	DH	-732.0	-734.5	-728.4		-664.0	-657.8	
ester								
methyl methanoate	WB	-355.5	-360.9	-359.9	-302.9	-301.7	-300.7	
ethyl methanoate	GA	-388.4	-394.9	-393.6		-304.8	-303.4	
propyl methanoate			-415.4	-414.0		-294.6	-293.2	
isopropyl methanoate			-433.5	-431.7		-310.7	-308.8	
methyl ethanoate	CC	-408.8	-413.3	-411.1	-321.4	-325.0	-322.8	
methyl propanoate	GA	-432.5	-435.7	-433.0		-316.0	-313.3	
ethyl ethanoate	DH	-444.1	-447.2	-444.6	-328.5	-328.0	-325.4	
oxiranone			-176.2	-174.7		-149.8	-148.3	
2-oxetanone	WB/CC ^o	-282.9	-285.9	-283.3	-238.3	-225.5	-223.0	
dihydro-2(3H)-furanone	CC	-366.5	-372.3	-369.1		-278.1	-274.8	
tetrahydro-2H-2-pyranone	DH	-379.6	-386.2	-382.7		-259.2	-255.6	
carboxyl derivatives								
acetyl chloride	CC	-242.8	-242.5	-240.2	-205.1	-204.8	-202.6	
acetic anhydride	DH	-573.5	-578.9	-574.0	-474.3	-474.5	-469.6	
succinic anhydride	DH	-527.9	-528.4	-522.9		-450.4	-444.9	
overall average			2.9	2.9		3.0	4.5	2.0
alcohols			2.9	2.5		3.7	5.3	1.4
ethers			2.9	2.4		3.5	3.9	2.1
cycloethers			3.1	3.3		2.4	2.5	
peroxides			2.4	2.8				
aldehydes			2.1	3.0		3.9	7.4	3.4
ketones			2.7	3.5		3.0	3.9	1.8
carboxylic functional groups			3.5	3.2		1.0	2.5	

^a kJ/mol. ^b CC, ref 2; WB, ref 1; DH, literature cited in ref 8; GA, values determined by group additivity method in ref 8. ^c A constant value of 2.5 kJ/mol has been subtracted from the G3 energy along with an additional 1.2 kJ/mol for each rotatable carbon-carbon bond. ^d Explicit calculation of all gauche conformers gives a value of -142.1 kJ/mol. ^e Group additivity estimates $\Delta H_f^\circ = -317.6$ kJ/mol and $\Delta G_f^\circ = -134.8$ kJ/mol. ^f Group additivity estimates $\Delta H_f^\circ = -338.3$ kJ/mol and $\Delta G_f^\circ = -126.5$ kJ/mol. ^g Correction is from the G3MP2 energy. ^h Group additivity estimates $\Delta H_f^\circ = -358.9$ kJ/mol and $\Delta G_f^\circ = -118.2$ kJ/mol. ⁱ Group additivity estimates $\Delta H_f^\circ = -331.5$ kJ/mol and $\Delta G_f^\circ = -170.4$ kJ/mol. ^j Group additivity estimates $\Delta H_f^\circ = 321.3$ kJ/mol and $\Delta G_f^\circ = -163.3$ kJ/mol. ^k The enthalpy is from reference 19; entropy from ref 8. ^l Explicit calculation of all gauche conformers gives a value of -106.3 kJ/mol. ^m Explicit calculation of all gauche conformers gives a value of -138.8 kJ/mol. ⁿ Reference 1 also gives -101.3 kJ/mol for the enthalpy. ^o Enthalpy from ref 1; entropy from ref 2; the latter gives a value of -297.1 kJ/mol for the enthalpy.

less than 2 kJ/mol. Are the errors in the literature values rather than the computations? An answer to this question is difficult

because the paucity of experimental data and the escalating size of these molecules make it difficult to examine a series of

compounds as we have done in several other cases. Results comparable to ours have been reported for oxetane and tetrahydrofuran³⁰ and many of these cycloethers have been examined by Notario, et al.³¹ using the G3MP2B3 model chemistry. Our results are within 2, and often 1, kJ/mol of theirs for most examples. This includes the aforementioned 1,3-dioxolane and trioxane.

The mean deviation for the free energies is somewhat higher than that observed for the enthalpies; however, correction brings the mean deviation to just over 2 kJ/mol. In applying the corrections, we make no compensation for the presence of the oxygen; the standard 1.2 kJ/mol per rotatable bond is applied to each carbon–carbon or carbon–oxygen bond whose rotation affords a different conformer. The first member of the 1-methoxyalkane homologous series, methoxymethane is not improved by correction, but the subsequent members of the series for which we have data are. The one free energy that is outside our ideal range is that of methyl *tert*-butyl ether which is not correctable. Isopropyl *tert*-butyl ether is also not correctable and lies at the border of our ideal range. The first has a computed free energy that is already lower than experiment and correction would make the result worse while the latter is higher than experiment.

We have included several peroxides and hydroperoxides for which there is enthalpy data, but no entropy data. Our mean absolute deviation for these enthalpies excludes those of ethyl and propyl hydroperoxides for which our values differ from experiment by 45 and 65 kJ/mol, respectively. They are within two kJ/mol of the computed results published by Lay and Bozzelli.³² If the experimental results are to be believed, the propyl hydroperoxide is more stable than the isopropyl, a result that does not obtain with any other functionalized three carbon system. We have calculated the butyl hydroperoxide for which no experimental data exists and observe a smooth progression through the three straight chain homologues with differences between the enthalpy lying very close to the Benson group equivalents. Further, our value for isopropyl hydroperoxide is approximately 20 kJ/mol lower than the value for the isomeric propyl hydroperoxide, about the same as the difference between 1- and 2-propanol. Hence, we conclude that the values for ethyl and propyl hydroperoxide given in reference 1 are incorrect. It is probable that the value for isopropyl hydroperoxide in reference two is also in error, although not as significantly.

For the aldehydes and ketones, the enthalpy mean deviation lies within the ideal and would be even smaller if ethanal were excluded. Our determination is 6–7 kJ/mol too high and is one of two compounds within this group that have large deviations. Because the number of compounds in each group having both experimental enthalpies and entropies is small, we have included some of the longer chain aldehydes for which group additivity data is available. The homologous straight chain aldehydes were studied by da Silva and Bozzelli³³ using the G3, G3B3, and CBS-APNO model chemistries. They found a value for ethanal (–166.2 kJ/mol) which is closer to our result than it is to experiment. They also determined the enthalpy for heptanal, reporting a value of –268.6, nearly identical to our result and 5 kJ/mol below the experimental. It is possible that the

experimental enthalpy for heptanal is too high as the difference between it and pentanal is just 36.5 kJ/mol, less than the equivalent of two methylene groups. If we assume that the value computed in this work and da Silva is correct, a rational sequence of enthalpies progressing from one aldehyde to the next homolog by a normal methylene equivalent is obtained. Unfortunately, in harmonizing the enthalpy, the free energy results are made worse.

The computed free energies of the aldehydes have the largest mean deviation of all of the oxygen-containing compounds. Although correction improves the result, the mean deviation is still larger than the other groups. Determination of the free energy corrections ignores that a functional group is present. We simply count the number of carbon–carbon bonds whose rotation affords a different conformer and multiply by 1.2 kJ/mol as we did for the alkanes. The one bond that is excepted from this count is the bond to the α carbon atom of a ketone (it is counted for the aldehydes). The procedure works well for the low molecular weight aldehydes but deviates significantly for the longer homologs.

Enthalpies and free energies for the ketones fall within our ideal range with few exceptions. Our values for both cyclopropanone and cyclobutanone are higher than those found in the literature. In the case of the former, we note that the error bar is larger than common for most compounds which we have examined. Rogers et al.²⁷ reported a value of 16.3 kJ/mol that is much closer to experimental value. This was done by G2 atomization method and compares with our result of 17.3 kJ/mol using the same procedure. This seems to be one instance in which atomization affords better results. For cyclobutanone, we could improve the result if we found a lower energy conformation for cyclobutanone. Our structure and those in the CCCBDB² output show no puckering as cyclobutane does. Starting with a variety of puckered structures and removing all symmetry constraints affords, in the end, a planar cyclobutanone. This is an issue because ref 1 gives two values for the cyclobutanone enthalpy differing by nearly 10 kJ/mol. We have chosen the value that is closest to ours but recognize that the error may be much larger. There is a similar range of values for cyclohexanone which like cyclohexanol is computed to have a significantly lower enthalpy and free energy than determined by experiment.

There is a paucity of data for the carboxylic acids and their derivatives. There is little difference between the mean absolute deviations of the enthalpies of these compounds determined by the G3 and G3MP2 models. However, when we examine individual groups, we find that the G3 deviation is nearly half that of G3MP2, while for the esters these values are reversed. Politzer et al.²⁶ have published a density functional enthalpy for methyl ethanoate that is somewhat closer to experiment than our value. Sumathi and Green²⁸ have reported a value for 2-methylpropanoic acid which is 2.7 kJ/mol lower than our G3 result. They have also examined several of the esters that we have listed in Table 4 using corrected CBS-Q performed calculations. In only one case, that of ethyl ethanoate, do our results deviate by more than 2 kJ/mol from theirs. The most comprehensive examination of these compounds was published recently by Liu and Cheng.³⁴ They examined methanoic acid and the next 18 homologues of this compound along with the methyl esters of the first 15. They employed both density functional methodologies similar to that which we investigated

(30) Wijaya, C. D.; Sumathi, R.; Green, W. H., Jr. *J. Phys. Chem. A* **2003**, *107*, 4908.

(31) Notario, R.; Roux, M. V.; Castaño, O. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3717.

(32) Lay, T. H.; Bozzelli, J. W. *J. Phys. Chem. A* **1997**, *101*, 9505.

(33) Da Silva, G.; Bozzelli, J. W. *J. Phys. Chem. A* **2006**, *110*, 13058.

(34) Liu, M. H.; Cheng, S.-R. *THEOCHEM* **2006**, *763*, 149.

TABLE 5. Experimental Enthalpies and Free Energies of Formation^a and Deviations for Aliphatic Compounds Containing One or More Sulfur Atoms and Determined by G3 and G3MP2 Model Chemistries Using the Bond Separation Method for the Thiols and Disulfides; Semi-homodesmotic Reactions for the Sulfides

molecule	source ^b	enthalpies of formation			free energies of formation			corrected ^c
		literature	G3	G3MP2	literature	G3	G3MP2	
thiols								
ethanethiol	CC	-46.0	-48.4	-48.2	-4.5	-4.3	-4.1	-4.8
1-propanethiol	CC	-68.6	-70.6	-70.2	1.5	4.3	4.7	2.6
1-butanethiol	DH	-88.1	-91.9	-91.3	11.2	13.8	14.3	10.9
1-pentanethiol	WB	-110.8	-113.4	-112.7		23.0	23.8	18.9 ^d
1-hexanethiol	DH	-129.0	-134.9	-133.9	28.0	32.3	33.2	27.0
1-heptanethiol	DH	-150.0		-155.2	36.0		42.7	36.2 ^e
1-octanethiol	DH	-170.2		-176.5	44.9		52.2	44.5 ^e
1-nonanethiol	DH	-190.8		-197.8	53.3		61.7	52.8 ^e
1-decanethiol	DH	-211.5		-218.9	61.7		71.4	61.3 ^e
2-propanethiol	CC	-76.9	-79.7	-79.2	-3.2	-3.5	-3.0	-4.0
2-butanethiol	DH	-96.9	-102.1	-101.4	4.9	5.1	5.8	3.4
2-methyl-1-propanethiol	DH	-97.2	-100.4	-99.8	5.7	6.9	7.4	6.9
2-methyl-2-propanethiol	DH	-109.6	-115.6	-114.4	0.7	-6.1	-4.9	-6.1
2-methyl-2-butanethiol	CC	-126.9	-134.5	-133.0	9.5	5.9	7.4	5.9
sulfides								
methyl ethyl sulfide	CC	-60.3	-61.5	-61.2	10.8	12.2	12.5	9.8
methyl propyl sulfide	DH	-81.8	-82.7	-82.1	18.5	21.4	22.0	17.8
methyl butyl sulfide	DH	-102.2	-104.2	-103.5	26.8	30.7	31.5	25.9
methyl pentyl sulfide	DH	-122.8	-125.7	-125.7	35.3	40.0	40.3	33.9
methyl isopropyl sulfide	DH	-90.4	-92.8	-92.1	13.6	12.8	13.6	9.2
2-methyl-2-thiomethylpropane	DH	-121.0	-127.0	-125.7	19.4	11.8	13.2	10.6
diethyl sulfide	DH	-83.7	-84.7	-83.8	17.7	20.9	21.8	17.3
ethyl propyl sulfide	DH	-104.6	-106.4	-105.3	23.7	28.3	29.4	23.4
ethyl butyl sulfide	DH	-125.2 ^d	-128.0	-126.7	32.2	37.5	38.8	31.4
dipropyl sulfide	DH	-125.4	-129.2	-127.9	33.4	36.5	37.7	31.8
diisopropyl sulfide	DH	-141.3 ^e	-149.1	-147.4	27.3	18.6	20.3	16.3
thiacyclopropane	DH	82.2	77.0	77.9	96.9	91.4	92.3	
thiacyclobutane	DH	61.0	62.0	63.2	107.5	107.2	108.4	
thiacyclopentane	DH	-34.2	-34.2	-32.6	45.7	45.6	47.2	
thiacyclohexane	DH	-63.3	-65.8	-64.1	53.2	49.3	51.0	
disulfides								
dimethyl disulfide	DH	-24.4	-29.5	-29.3	14.5	11.2	11.4	
methyl ethyl disulfide	WB	-49.4	-54.7	-53.9		14.9	15.7	
diethyl disulfide	DH	-74.6	-80.0	-78.6	22.4	20.2	21.6	
ethyl tert-butyl disulfide	DH	-74.6	-80.0	-78.6	22.4	20.2	21.6	
dipropyl disulfide	DH	-117.2		-120.8	37.2		40.7	
dibutyl disulfide	DH	-158.4		-164.3	54.1		58.8	
overall			3.6	3.4		3.1	3.7	2.0
thiols			4.1	4.3		2.5	4.2	1.4
sulfides			2.8	2.1		3.7	3.9	2.8
disulfides			5.3	4.4		2.5	2.3	

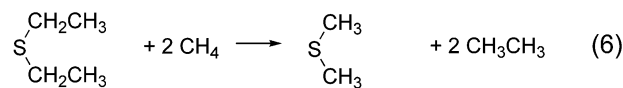
^a kJ/mol. ^b WB, ref 1; CC, ref 2; DH, literature cited in ref 8. ^c A constant value of 0.5 kJ/mol is subtracted from the G3 energy for the sulfur in the thiols, but none in the sulfides. An additional 1.2 kJ/mol is subtracted for each rotatable carbon-carbon bond in both the thiols and the sulfides. ^d Explicit calculation of all gauche conformers gives a value of 20.0 kJ/mol. ^e The correction is based on the G3MP2 energy. ^f Reference 1 gives a value of 127. kJ/mol. ^g Reference 1 lists two additional values of 142 and 143 kJ/mol.

in our previous paper in this series¹⁰ and ab initio at a level well below that which we are using. The results do not compare in accuracy with those which we report in Table 4 and underscores the importance of using ab initio methodologies that have significant polarization functions.

The free energies are, in fact, closer to experiment than the enthalpies. Rotation around the C-OR(H) bond from the syn to the anti conformation is higher in energy than rotation around carbon-carbon bonds so that the population of the latter conformation is limited and no correction is required. Larger molecules should require correction for rotation about the carbon-carbon bond and we assume that the bond to the α carbon should be counted as it is for the aldehydes, but we have no data to corroborate this. There are only two carboxylic acids for which we have literature values for both enthalpies and free energies: methanoic and ethanoic acid. These values are predicted quite accurately and hence make our statistics look quite good. Sumathi and Green²⁸ also computed entropies for

the esters that they examined and we have used these to compute free energies. Most of these agree with our results within 2 kJ/mol, and the two exceptions differ by less than 3.

Sulfur. The results for sulfur compounds are shown in Table 5. We have used the isodesmic process to compute enthalpies and free energies of the thiols and disulfides and the semi-homodesmotic process for the sulfides as illustrated in eq 6 for diethyl sulfide. There are conflicting reasons for using the semi-homodesmotic equations to compute thermodynamic data of the sulfides. The enthalpies are improved by about a 0.5 kJ/mol. The errors in the uncorrected free energies are increased relative to those computed using isodesmic equations; however, the mean of the corrected energies is approximately the same either way.



Gomes and Ribeiro da Silva³⁵ have reported enthalpies for several of these compounds determined by the atomization method and using four different model chemistries. Our results have consistently come in at a slightly lower energy even when we compare our atomization results. The overall mean absolute deviation for the enthalpies of the sulfur compounds is just below the cutoff for the ideal range. Two groupings, the thiols and disulfides, are above this cutoff value. There are two issues which are responsible for the thiols being just over the cutoff of the ideal. The first is the two tertiary thiols. Elimination of these two from the computation of the average brings the G3 mean deviation into the ideal and leaves the G3MP2 just above. The second is in the long-chain thiols. Looking at the homologous series from ethanethiol through 1-decanethiol, we see that agreement with experiment for both the enthalpies and free energies is quite good at the initial stage but becomes increasingly larger as the chain length increases. This same trend was observed with the alcohols, and it is possible that a system of corrections for the long-chain molecules is needed for enthalpies as well as entropies.

The sulfides are mostly well described by computation with three notable exceptions. The first is 2-methyl-2-thiomethylpropane, a functionalized tertiary compound whose errors can be seen as reflecting those in the parent 2-methyl-2-propanethiol. The second is diisopropyl sulfide whose errors can be understood by referring back to the parent thiols. The difference between 1- and 2-propanethiol is approximately 8 kJ/mol in experiment and 10 kJ/mol in our computation. The corresponding difference between the propyl and isopropyl thiols is 16 kJ/mol for experiment and 20 for computed enthalpies. There is a consistence in both for the effects of increasing substitution, however, computation exaggerates the effect. The cyclic sulfides are well described by computation with the exception of the three atom heterocycle.

Correction of the free energies is similar to that which we described for the amines and alcohols except that we use a constant of 0.5 kJ/mol for rotation around the bond adjacent to the sulfur and the standard 1.2 kJ/mol for all other rotatable bonds. This brings the free energies within 2 kJ/mol in all cases and in most cases to less than 1 kJ/mol. The remaining thiols are accurately described with the exception of the two tertiary compounds.

Finally, we have looked at several disulfides for which experimental enthalpy and entropy data is available. Several of these also have entropies reported. The mean deviation for the enthalpies is just outside our ideal range while that of the free energies are within. The enthalpies are consistently lower than experiment by about 4–5 kJ/mol. This consistent error suggests a systematic error in one of the experimental values used in the bond separation reaction. Most likely this is dihydrogen disulfide. Several groups have looked at the disulfides, most frequently in conjunction with the determination of the HSS–H bond dissociation energy. Denis³⁶ computed the formation enthalpies of both dihydrogen disulfide and the corresponding radical. The enthalpy obtained for the former deviates substantially from the value that we have used from reference 2. The D° computed from this data, however, is consistent with the value computed by two other groups: do Couto et al.³⁷ and

Mo et al.³⁸ which is approximately 15 kJ/mol higher than the experimental value given by Luo.³⁹ That experimental value has a large error bar and it is clear that further work on these compounds is required to obtain definitive values.

Fluorine. The role of fluorinated and polychlorinated compounds in refrigeration and upper atmosphere chemistry has generated a significant number of computational studies.⁴⁰ Most of this has focused on the one- and two-carbon molecules; however, a recent paper by Kormos et al. has examined both the experimental and computational problems associated with the lower molecular weight alkyl fluorides.⁴¹ Difficulties in obtaining consistent and accurate data are found even with the simplest of the organofluorine compounds, fluoromethane. The Webbook¹ reports two values, –234.3 and –247.0 kJ/mol. A comprehensive review of the literature showed a range of experimental values ranging from 225 to 255 kJ/mol.^{2,8,42,43} Computational estimates^{40d,44} were more closely focused on the range between 234 and 240 kJ/mol, and these are in accord with our G3 value of –237.2 determined by atomization. As the experimental value, we have used –234.3 kJ/mol from ref 1 which matches very closely the 233.9 kJ/mol of Luo and Benson.⁴³ The value appears to be more rigorously derived, and we have found the mean absolute deviations in our comparison set are closer to a minimum than with any other value. This uncertainty in the enthalpy for CH₃F may have been the impetus for the use of CF₄ in the bond separation equations by Haworth et al.^{40d} as the value of the latter is more precisely known.¹

We have calculated our enthalpies using both CH₃F and CF₄ as the reference. The enthalpies of the fluoromethanes CH_xF_{4–x} calculated using CF₄ as the reference are closer to experiment than those calculated from CH₃F; however, molecules having two or more carbon atoms are more accurately described using the latter regardless of the number of fluorine atoms. Consequently, we have used fluoromethane rather than tetrafluoromethane to calculate the values found in Table 6. Using CF₄ in the bond separation equations affords us the opportunity for an independent determination of the DH_f of fluoromethane: –236.0 (G3) and –236.2 (G3MP2) kJ/mol. These are quite close to the values computed by the atomization method as well as the experimental value we have used in the bond separation reactions.

The results are shown in Table 6 along with a summary of the relative performance. The results for the chlorofluoroalkanes are included in the next section with the chlorine compounds. We note that the overall mean deviations do not fall within our ideal category for either the enthalpies or free energies but are

(38) M6, O.; Yáñez, M.; Eckert-Maksiaë, M.; Maksiaë, Z. B.; Alkorta, I.; Elguero, J. *J. Phys. Chem. A* **2005**, *109*, 4359.

(39) Luo, Y.-R. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRC Press: Boca Raton, 2003.

(40) For leading references, see (a) Cameron, M. R.; Bacskey, G. B. *J. Phys. Chem. A* **2000**, *104*, 11212. (b) Bauschlicher, C. W., Jr.; Ricca, A. *Chem. Phys. Lett.* **1999**, *315*, 449. (c) Schneider, W. F.; Wallington, T. J. *Phys. Chem. A* **1993**, *97*, 12783. (d) Haworth, N.; Smith, M. H.; Bacskey, G. B.; Mackie, J. C. *J. Phys. Chem. A* **2000**, *104*, 7600. (e) Lazarov, Y. G.; Promistis, A. V.; Papadimitriou, V. C. *J. Phys. Chem. A* **2001**, *105*, 6729. (f) Espinosa-Garcia, J. *Chem. Phys. Lett.* **1996**, *250*, 71.

(41) Kormos, L.; Liebman, J. F.; Cramer, C. J. *J. Phys. Chem.* **2004**, *17*, 656.

(42) (a) Liebman, J. F.; Samoes, J. A. M.; Slayden, S. W. *Struct. Chem.* **1995**, *6*, 65. (b) Yaws, C. L.; Chiang, P.-Y. *Chem. Eng.* 1988, Sep 26, 81.

(43) Luo, Y.-R.; Benson, S. W. *J. Phys. Chem.* **1997**, *101*, 3042.

(44) (a) Kormos, L.; Liebman, J. F.; Kramer, C. J. *J. Phys. Chem.* **2004**, *17*, 656. (b) Lazarov, Y. G.; Promistis, A. V.; Papadimitriou, V. C. *J. Phys. Chem. A* **2001**, *105*, 6729. (c) Espinosa-Garcia, J. *Chem. Phys. Lett.* **1996**, *250*, 71.

(35) Gomes, J. R. B.; Ribeiro da Silva, M. A. V. *J. Phys. Chem. A* **2004**, *108*, 11684.

(36) Denis, P. A. *Chem. Phys. Lett.* **2003**, *382*, 65.

(37) Do Couto, P. C.; Cabral, B. J. C.; Simões, J. A. M. *Chem. Phys. Lett.* **2006**, *421*, 504.

TABLE 6. Experimental Enthalpies and Free Energies of Formation^a and Deviations for Aliphatic Halocarbons Determined by G3 and G3MP2 Model Chemistries Using the Bond Separation Method and Fluoromethane as the Basis

molecule	source	enthalpies of formation			free energies of formation		
		literature	G3	G3MP2	literature	G3	G3MP2
fluoroethane	LB/DH	-276.6	-271.2	-270.8	-224.6	-219.3	-218.8
1-fluoropropane	DH	-285.9	-292.0	-291.3	-204.9	-209.0	-208.3
2-fluoropropane			-313.2	-312.3		-229.6	-228.7
1-fluorobutane			-313.1	-312.3		-199.2	-198.5
2-fluorobutane			-334.8	-333.4		-220.1	-218.8
1-fluoro-2-methylpropane			-320.2	-319.3		-205.0	-204.0
2-fluoro-2-methylpropane			-357.8	-355.9		-239.0	-237.1
difluoromethane	CC	-452.2	-447.6	-447.7	-424.6	-420.1	-420.2
trifluoromethane	CC	-696.7	-691.2	-691.1	-662.3	-656.9	-656.8
tetrafluoromethane	CC	-933.2	-926.5	-925.7	-888.5	-882.1	-881.3
1,1-difluoroethane	CC	-500.8	-501.6	-500.7	-443.3	-444.2	-443.2
1,1,1-trifluoroethane	DH	-744.6	-750.7	-748.9	-677.7	-684.1	-682.3
1,1,2-trifluoroethane	DH	-664.8	-665.8	-664.6	-605.1	-604.0	-602.7
fluoroethene	CC	-140.1	-141.0	-140.3	-123.4	-124.3	-123.6
1,1-difluoroethene	CC	-336.4	-348.2	-346.3	-312.9	-324.5	-322.6
1,1,2-trifluoroethene	DH	-490.4	-494.9	-492.6	-464.1	-468.7	-466.4
1,1,2,2-tetrafluoroethene	CC	-659.5	-669.4	-666.3	-624.7	-634.6	-631.6
overall mean deviation			5.3	4.4		5.1	4.3
monofluorohydrocarbons			4.1	3.8		3.4	3.1
polyfluorohydrocarbons			5.7	4.6		5.6	4.8
fluoroalkenes			6.8	4.8		6.8	4.8

^a kJ/mol. ^b CC, ref 2; WB, ref 1; DH, literature cited in ref 8; GA, values determined by group additivity method in ref 8. ^c The enthalpy is from ref 43; entropy is taken from ref 8. ^d Enthalpy is -133.9 kJ/mol in ref 19.

in the acceptable category. Only three compounds are in the ideal category, and two have deviations placing them outside the acceptable. We will first examine the monofluoroalkanes and then the polyfluoro compounds. We noted previously that there is uncertainty in the literature concerning several of the enthalpies for these compounds.

Examination of Table 6 shows that there are few experimental free energies available with which to compare our computed results. In the case of fluoroethane, our computed value is higher than the literature value while that of 1-fluoropropane is much lower. Correcting for multiple conformations should further lower this result. Since there are no other compounds with which to compare computational free energies, we have not included corrections for these compounds even though explicit calculation of all conformers for several of the low molecular weight compounds shows that there should be an effect.

Domalski and Hearing⁸ cite a value of -261.5 kJ/mol for the experimental value of fluoroethane; a somewhat larger value of -263.2 kJ/mol appeared in the earlier literature.⁴⁵ More recently, Luo and Benson⁴³ as part of their work on fluoromethane derived a value of -276.6 kJ/mol which brings our results within the acceptable range. Other computational results are close to our value including those of Haworth et al.^{40d} and Berry.⁴⁶

Luo and Benson have also proposed a revision of the experimental value of 1-fluoropropane to which Smith⁴⁷ has offered a reinterpretation. Both values, -298.22 and -295.7 kJ/mol, respectively, are higher than that in Table 6 and higher than our computation of -290.7 kJ/mol. For the isomeric 2-fluoropropane, no experimental value has been given in our primary sources, however, Luo and Benson and Smith⁴⁷ have suggested values of -318.8 and -316.8 kJ/mol, respectively.

These compare with our values of -312.8 kJ/mol and another computational value of -318.8 determined by Kormos^{44a} using the G3 multi-coefficient method. These form a relatively tight band giving some assurance that the correct value lies in this range. In contrast, the derived enthalpies for tert-butyl fluoride determined by Luo and Benson and Smith differ by more than 10 kJ/mol. Both values, -376.1 and -365.9 kJ/mol, are lower than our computational determination of -357.4. Kormos^{44a} reports a value of -359.8 kJ/mol. No literature values are available for the other isomeric butyl fluorides; however, the values found in Table 6 appear reasonable in that they follow the relative stabilities of other butyl compounds and by approximately the same amount.

The deviations for the polyfluoromethanes are outside the ideal range, but within acceptability for di and trifluoromethane. As we noted earlier in this discussion, improvement is noted when the calculation is done using tetrafluoromethane as the component having the C-F bond. The bond separation reaction becomes



Obviously, tetrafluoromethane itself cannot be calculated by this method. The results are shown in Table 7 and afford deviations that are within our ideal range for all one-carbon molecules.

Other computational determinations for tetrafluoromethane have come closer to the mark. Bauschlicher et al.⁴⁸ obtained a value of -933.5 kJ/mol using coupled cluster atomization energies and Politzer⁴⁹ reports a value of 931.4 kJ/mol determined by density functional calculations followed by empirical atomic correction terms.

(45) Chen, S. S.; Rodgers, A. S.; Chao, J.; Withoit, R. C.; Zwolinski, B. *J. J. Phys. Chem. Ref. Data* **1975**, *4*, 441.

(46) Berry, R. J.; Ehlers, C. J.; Burgess, D. R., Jr.; Zachariah, M. R.; Nyden, M. R.; Schwartz, M. *THEOCHEM* **1998**, *422*, 89.

(47) Smith, D. W. *J. Phys. Chem. A* **1998**, *102*, 7086.

(48) Bauschlicher, C. W., Jr.; Ricca, A. *Chem. Phys. Lett.* **1999**, *315*, 449.

(49) Politzer, P.; Ma, Y.; Lane, P.; Concha, M. C. *Int. J. Quantum. Chem.* **2005**, *105*, 341.

TABLE 7. Experimental Enthalpies and Free Energies of Formation^a and Deviations for Aliphatic Halocarbons Determined by G3 and G3MP2 Model Chemistries Using the Bond Separation Method and Tetrafluoromethane as Reference

molecule	source ^b	enthalpies of formation			free energies of formation		
		literature	G3	G3MP2	literature	G3	G3MP2
fluoromethane	WB	-234.3	-236.0	-236.2	-210.4	-212.0	-212.2
difluoromethane	CC	-452.2	-450.9	-451.4	-424.6	-423.3	-423.8
trifluoromethane	CC	-696.7	-696.3	-696.7	-662.3	-661.8	-662.2
1,1-difluoroethane	CC	-500.8	-505.0	-504.4	-443.3	-447.4	-446.8
1,1,1-trifluoroethane	DH	-744.6	-755.7	-754.5	-677.7	-688.9	-687.7
1,1,2-trifluoroethane	DH	-664.8	-670.9	-670.1	-605.1	-608.8	-608.1
fluoroethene	CC	-140.1	-142.7	-141.9	-123.4	-126.0	-125.2
1,1-difluoroethene	CC	-336.4	-351.5	-349.8	-312.9	-327.7	-326.0
1,1,2-trifluoroethene	DH	-490.4	-499.9	-498.0	-464.1	-473.5	-471.6
1,1,2,2-tetrafluoroethene	CC	-659.5	-676.1	-673.6	-624.7	-641.1	-638.6
overall mean deviation			6.9	5.8		6.6	5.6
one carbon compounds			1.1	0.9		1.1	0.9
Two carbon compounds			9.3	7.9		8.9	7.6

^a kJ/mol. ^b CC, ref 2; WB, ref 1; DH, literature cited in ref 8.

Of the polyfluoroethanes that we have examined, only the G3 1,1,1-trifluoroethane falls outside the ideal; nevertheless, both the enthalpy and free energy are acceptable. Computations by other groups have afforded values between 745 and 750 kJ/mol,^{40d,46,50} and it is probable that the actual value lies in this range. Both 1,1-difluoroethane and 1,1,2-trifluoroethane are in the ideal range. Computations for two of the fluoroethenes that we have examined, fluoroethene and 1,1,3-trifluoroethene, give enthalpies and entropies that lie within the ideal for both G3 and G3MP2. In contrast, our values for 1,1-difluoroethene are much lower than the literature values and are outside the acceptable. Haworth et al.^{40d} obtained an enthalpy lower than ours and cited the same experimental energy. We used the CCCBDB value because of the associated entropy data and also because it claims the smallest uncertainty. Reference 1 lists three additional values ranging from -325 to -344 kJ/mol. The last mentioned value is very close to our own result of -347.3 kJ/mol but has a 10 kJ/mol error bar.

For tetrafluoroethene, G3MP2 does provide a result that is within 8 kJ/mol of experiment, but G3 does not. In an examination of the enthalpies of formation of tetrafluoromethane and tetrafluoroethene, Bauschlicher et al.⁴⁸ employed CCSD-(T) atomization energies extrapolated to the complete basis set limit. Their result for the former, 933.5 kJ/mol, missed the experimental value by only 0.3 kJ/mol. In contrast, their value for the latter showed a larger error than those which we are reporting. They examined critically the errors in the calculation and thermochemistry and concluded that "the experimental value has a far larger error bar than believed." They found that their G3 computed value for the enthalpy of this compound was within the normal errors for the G3 method.

Chlorine. As a group, the alkyl chlorides have one of the worst averages of any family of compounds that we have examined with a mean absolute deviation of 5.1 kJ/mol for the G3 enthalpies and 4.4 kJ/mol for the G3 free energies. We have divided these into four groups and of these only the chlorofluoroalkanes have enthalpies that are within ideal. For the free energies, two of the groups have averages within ideal: monochloro- and chlorofluoroalkanes. Our results are reported in Table 8. If we strike the six compounds having enthalpy errors outside the acceptable range, the mean deviation moves into our ideal range for the enthalpies and free energies for all four groups of compounds with one exception: the chloroalkene free

energies. The six compounds are 2-chloro-3-methylbutane, 1,2-dichloroethane, 1,2-dichloroethene, tetrachloromethane, 1,1,2,2-tetrachloroethene, and trichlorofluoromethane. We will examine each of the four groups of organochlorine compounds in turn examining more thoroughly our problem children along with the remainder of their group.

We have computed all of the chloroalkanes having two to five carbon atoms plus the ring compounds. Examining the homologous 1-chloroalkanes, we find good agreement with experimental enthalpies and reasonable agreement with the experimental free energies. The latter are substantially improved by adding a correction factor of 2.5 kJ/mol for rotation adjacent to chlorine and 1.2 kJ/mol for each additional rotatable carbon-carbon bond. The errors for the remaining compounds are larger, and correction of the free energies affords larger, not smaller deviations. Because of the paucity of experimental data for these compounds, we are not suggesting protocols for the correction of the free energies to include those higher energy conformers that would be expected to have a significant population at 298 K. Indeed, we note that our computed free energies are lower in energy than the experimental and inclusion of corrections would only make the errors larger. Further work is required with these compounds.

We advance two hypotheses to account for these results, neither of which can be proved at the level of the analysis employed in this paper. The first is that the model chemistries we have employed simply cannot cope with chlorine vibrational frequencies which are needed for the entropy calculations (and probably also fluorine, since we reported these same errors in the previous section). Is it the optimization/frequency analysis? Both the G3 and G3MP2 frequencies are run at the Hartree-Fock level. In our previous paper,¹⁰ we examined three model chemistries that employed density functional optimizations and frequencies. The mean absolute deviations from G3B3 and G3MP2B3 were slightly smaller than those we report here, but still larger than ideal. In contrast, CBS-QB3 gives a mean deviation that is outside our acceptable range for halogenated compounds, so that use of density functional frequencies is probably not the solution, but the question remains unresolved.

Our second hypothesis is to assume that our computed enthalpies are closer to the true values than are the experimental values. If we make this assumption and use our computational value as the experimental energy, a new set of free energies are obtained which are much closer to our computational free

(50) Olleta, A.; Lane, S. I. *Phys. Chem. Chem. Phys.* **2001**, *3*, 811.

TABLE 8. Experimental Enthalpies and Free Energies of Formation^a and Deviations for Aliphatic Halocarbons Determined by G3 and G3MP2 Model Chemistries Using the Bond Separation Method and Fluoromethane as the Basis

molecule	source ^b	enthalpies of formation			free energies of formation			
		lit.	G3	G3MP2	lit.	G3	G3MP2	corrected ^c
monochloro								
chloroethane	CC	-112.3	-112.3	-112.0	-60.5	-60.6	-60.3	-60.6
1-chloropropane	CC	-131.9	-134.5	-134.2	-52.2	-51.7	-51.3	-54.2
1-chlorobutane	DH	-154.6	-155.8	-155.3	-46.0	-42.2	-41.7	-45.9
1-chloropentane	DH	-175.2	-177.4	-176.7	-37.5	-33.0	-32.3	-37.9
2-chloropropane	DH	-144.8	-148.5	-147.9	-61.3	-64.8	-64.2	
2-chlorobutane	WB	-166.7	-171.4	-170.7	-50.3	-56.5	-55.8	
2-chloropentane			-192.8	-191.9		-47.2	-46.3	
3-chloropentane			-193.0	-192.2		-47.0	-46.1	
1-chloro-2-methylpropane	DH	-159.4	-164.2	-163.7	-49.5	-49.4	-48.9	
1-chloro-2-methylbutane			-183.3	-182.7		-37.7	-37.1	
2-chloro-2-methylpropane	DH	-182.4	-187.8	-186.6	-63.1	-68.2	-67.0	
2-chloro-2-methylbutane	DH	-202.2	-208.4	-207.0	-56.3	-59.9	-58.5	
1-chloro-3-methylbutane	DH	-180.3	-182.1	-181.5	-43.5	-36.9	-36.3	-40.6
2-chloro-3-methylbutane	GA	-183.1	-196.3	-195.5	----	-48.9	-48.0	-59.9
1-chloro-2,2-dimethylpropane			-199.5	-198.5		-51.0	-49.9	
chlorocyclopropane			28.5	30.0		79.4	80.9	
chlorocyclobutane			-18.3	-16.9		66.3	67.8	
chlorocyclopentane			-117.4	-115.7		-1.8	-0.1	
chlorocyclohexane	DH	-163.0	-169.7	-167.9		-15.1	-13.3	
polychloro								
dichloromethane	CC	-95.0	-95.5	-95.1	-68.4	-68.9	-68.5	
1,1-dichloroethane	CC	-130.1 ^d	-138.3	-137.2	-73.3	-81.3	-80.2	
1,2-dichloroethane	CC	-126.8 ^e	-135.5	-134.8	-70.2	-77.8	-77.2	
1,2-dichloropropane	DH	-162.8	-173.6	-172.5	-79.1	-85.3	-84.2	
2,2-dichloropropane	GA	-176.7 ^f	-182.1	-180.1	-85.4	-90.2	-88.1	
1,3-dichloropropane	DH	-159.2	-159.6	-158.7	-75.4	-72.6	-71.7	
trichloromethane	CC	-102.7 ^g	-106.8	-105.4	-70.1	-73.9	-72.5	
tetrachloromethane	CC	-95.6	-108.5	-104.9	-53.1	-65.9	-62.4	
chloroalkenes								
chloroethene	CC	23.0	21.3	21.8	39.4	37.7	38.2	
1,1-dichloroethene	CC	2.3	-1.1	0.2	25.2	21.9	23.2	
(E)-1,2-dichloroethene	CC	6.1	0.4	1.6	28.5	20.9	22.1	
(Z)-1,2-dichloroethene	CC	4.1	-2.1	-1.1	26.6	18.7	19.7	
1,1,2-trichloroethene	CC	-19.1 ^h	-19.4	-17.4	6.7	6.4	8.4	
1,1,2,2-tetrachloroethene	CC	-12.4	-32.7	-29.8	21.6	2.1	3.4	
3-chloro-1-propene	WB/GA	-6.8	-2.0	-1.2	37.2	44.4	45.3	
chlorofluoroalkanes								
chlorofluoromethane	WB	-261.9	-263.0	-262.5	-236.6	-237.7	-237.2	
chlorodifluoromethane	WB	-481.6	-481.1	-479.8	-450.5	-450.1	-448.8	
chlorotrifluoromethane	WB	-710.0	-707.8	-705.5	-669.4	-667.4	-665.1	
dichlorofluoromethane	WB	-283.3	-286.5	-284.7	-252.8	-255.9	-254.2	
trichlorofluoromethane	WB	-288.7	-297.4	-293.5	-249.4	-257.9	-254.1	
dichlorodifluoromethane	CC	-491.6	-497.7	-494.3	-452.7	-458.9	-455.5	
1-chloro-1-fluoroethane	CC	-313.8	-312.2	-310.8	-258.6	-255.1	-253.7	
overall mean deviation			5.0	4.1		4.6	4.1	
monochloroalkanes			4.8	4.0		3.4	3.3	
polychloroalkanes			7.2	5.8		6.6	5.3	
chloroalkenes			6.1	5.4		6.8	6.4	
chlorofluoroalkanes			3.3	2.7		3.6	2.9	

^a kJ/mol. ^b CC, ref 2; WB, ref 1; DH, literature cited in ref 8; GA, values determined by group additivity method in ref 8. ^c Corrected values based on G3 value. Computed by subtracting a constant of 2.5 kJ/mol for the chlorine and additional 1.2 kJ/mol for each rotatable carbon-carbon bond. ^d Enthalpy is -127.6 kJ/mol in refs 1 and 19. ^e Reference 1 gives alternative values of -125.4 and -129 kJ/mol. ^f Reference 1 gives an alternate value of -173 kJ/mol for the enthalpy. ^g There are several experimental values in reference 1 ranging from 94 to 125 kJ/mol. ^h Enthalpy is -1.9 kJ/mol in ref 19.

energies. Without supporting data, this is a flight of fancy; however, as part of a study to determine the enthalpies of formation of vinyl chloride, allyl chloride, and the 1-chloropropenes, Colegrove and Thompson⁵¹ examined the enthalpies of formation of several other alkyl halides. They employed both atomization and bond separation reactions using several variations of the basic reaction that we have employed. On the basis of their results and error analysis, they concluded that the experimental enthalpy of formation of 2-chloropropane should be 149.0 kJ/mol, nearly identical to our result. If this is correct and we add a methylene increment of 20.6 kJ/mol we obtain

169.1 kJ/mol for 2-chlorobutane. This is within 2 kJ/mol of our computational result.

Only one of the four butyl chlorides, 1-chlorobutane, matches experiment. Two others have larger errors but are within our limits of acceptability, and 2-chlorobutane is outside of the acceptable range. Examination of the alcohols and amines shows that the differences between the 1- and 2-propyl and 1- and 2-butyl compounds are comparable. In the case of the fluorides this is not true; the butyl isomers have a larger difference than the propyl isomers. For the butyl chlorides, however, the difference is smaller. If we assume that the enthalpy for 1-chlorobutane is correct and that the difference between the

(51) Colgrove, B. T.; Thompson, T. B. *J. Chem. Phys.* **1997**, *106*, 1480.

propyl and butyl chlorides should be comparable, then 2-chlorobutane would have an enthalpy between 167 and 168 kJ/mol, which is nearly identical to that suggested in the previous paragraph using a different approach.

There are fewer literature values for comparison among the isomeric pentyl chlorides. Our results for 1-chloropentane and 1-chloro-3-methylbutane are quite good. The experimental value for 2-chloro-3-methylbutane is higher in energy than the computed value for the two unbranched secondary halides. This suggests that it should be in the mid to high -190 's which is approximately where our computed value is. Referring back to the alcohols, we note that 2-methyl-2-butanol is ~ 13 kJ/mol more stable than neopentyl alcohol. In contrast, the literature value for 2-chloro-2-methylbutane is within experimental error of our computed value for neopentyl chloride. At ~ 8 kJ/mol more stable than the latter, our computed result is probably closer to the actual value. Whether or not our results for these compounds are strictly correct, the relative energies are internally consistent with accepted notions of relative stability.

Of the eight polychloroalkanes, only two come into our ideal range, three are acceptable, and the other three unacceptable. For the most part, the errors in the free energies mirror those in the enthalpies suggesting that computation is determining the entropies correctly. The two dichloroethanes differ significantly from experiment. We have cited the values from ref 2 because there is associated entropy data. Data from ref 1 approximates these values; however, between the two there is a range of values for each compound in the range between 125 and 130 kJ/mol. In essence, the enthalpies for the two compounds are nearly identical. Our calculation shows 1,1-dichloroethane to be more stable which corresponds with the relative stability of the two difluoroethanes.^{40d} Parthiban et al.⁵² determined W1 enthalpies of formation for acetylene and halosubstituted acetylenes. From these they have suggested a revised ΔH_f° for 1,2-dichloroethane of -133.1 kJ/mol which is very close to our result. This suggests that our value for 1,1-dichloroethane is also close to the mark.

Of the three dichloropropanes, our computed value for 1,3-dichloropropane matches the experimental almost exactly. The other two differ significantly. Nevertheless, our value for 1,2-dichloropropane differs from that of 1,3-dichloropropane by just over 12 kJ/mol, approximately the same difference that is found between the primary and secondary alkyl halides that we examined earlier. Unless there is a destabilizing effect from the vicinal halogens on the former, the experimental enthalpy appears to be too high.

Finally, our computed value for tetrachloromethane is significantly higher than experiment. We have noted in the footnotes to Table 8 that there are a significant number of experimental values for this compound, some of which are closer to ours, however, most compilations are giving greater credence to the value that we have cited. Feller et al.⁵³ obtained a value for tetrachloromethane that matched the experimental value using coupled cluster computations and multiple corrections. Using G3 theory, Ma et al.⁵⁴ obtained a value that is within acceptability, presumably by the atomization method since it is close to our value for that method.

Removal of just one set of data from the chloroalkenes, that of 1,1,2,2-tetrachloroethene, drops the mean deviation for this group into the ideal range. The deviation for this compound is 20 kJ/mol, and there are no corroborating calculations by other workers to confirm or deny the validity of this calculation.

Finally, we examine the chlorofluoroalkanes. This is the only one of our groups in this section that has a mean deviation that falls into the ideal range without excluding very extraneous results. Only two compounds fall outside the ideal range: dichlorodifluoromethane and trichlorodifluoromethane. Ma et al.⁵⁴ calculated the enthalpy for dichlorodifluoromethane, obtaining a value of -500.3 kJ/mol. This is close to the result of Cameron and Bacskey⁵⁵ who report -501.2 kJ/mol also using the atomization method. These values are close to our atomization result of -499.6 , but none come as close as does our bond separation result of -496.9 kJ/mol. Nevertheless, it remains more than ten kJ/mol lower in energy than the literature result but the convergence of computational results suggests that the experimental results require additional work. Finally, we examine trichlorofluoromethane which is also computed to be about ten kJ/mol more stable than the experimental result. This is another substance for which ref 1 has multiple values, most of them even higher in energy than the one that we have used. Our result is nearly identical with that reported by Cameron and Bacskey^{40d} using the same methodology and much better than that reported by Berry et al.⁴⁶ using the G2 and CBSQ model chemistries. Whether additional improvements will bring the results closer to experiment remains to be seen.

Five of the six problematic compounds from this section have more than one halogen. It may be reasonable to conclude that G3 theory has difficulty with the poly halo compounds and that still higher level calculations are required to adequately describe these molecules. Nevertheless, a significant number are accurately computed and in the case of several others, it is quite possible that it is the experimental value which may be in error rather than the computational. It is clear that further work with these compounds is required and perhaps not just by computational chemists.

Bromine. The results for the organobromine compounds shown in Table 9 are G2 and G2MP2 rather than the G3 since neither Gaussian 98 nor Gaussian 03 will compute these compounds, despite published parameters for the basis sets.⁵⁶ Curtiss, et al.⁵⁷ have examined the ability of the Gaussian 3 model to compute enthalpies of formation for several bromine compounds, but have not included the free energies.

Like the chlorine compounds, G2 theory predicts lower enthalpies of formation than those found in the literature. These are within our ideal criteria for all alkyl bromides except tert-butyl bromide which drops into the acceptable category. Espinosa-Garcia⁵⁸ determined the enthalpy of 1-bromopropane using a hydrogenation reaction and obtained results that are with two kJ/mol of ours.

Similar results are found for the free energies. Because most of these are already lower than experiment, we have not corrected for multiple conformations. For the two examples where the free energies are higher, corrections would provide mixed results. In the case of 1-bromobutane, corrections similar

(52) Parthiban, S.; Martin, J. M. L.; Liebman, J. F. *Mol. Phys.* **2002**, *40*, 399.

(53) Feller, D.; Peterson, K. A.; de Jong, W. A.; Dixon, D. A. *J. Chem. Phys.* **2003**, *118*, 3510.

(54) Ma, N. L.; Lau, K.-C.; Chien, S.-H.; Li, W. K. *Chem. Phys. Lett.* **1999**, *311*, 275.

(55) Cameron, M. R.; Bacskey, G. B. *J. Phys. Chem. A* **2000**, *104*, 11212.

(56) Curtiss, L. A.; Redfern, P. C.; Rassolov, V.; Kedziora, G.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 9287.

(57) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **2005**, *123*, 124107.

(58) Espinosa-Garcia, J. *Chem. Phys. Lett.* **2003**, *377*, 607.

TABLE 9. Experimental Enthalpies and Free Energies of Formation^a and Deviations for Aliphatic Halocarbons Determined by G2 and G2MP2 Model Chemistries Using the Bond Separation Method

molecule	source ^b	enthalpies of formation			free energies of formation		
		literature	G2	G2MP2	literature	G2	G2MP2
bromoethane	DH	-64.0	-66.2	-65.9	-27.5	-28.5	-28.1
1-bromopropane	DH	-84.7	-88.9	-88.4	-19.1	-20.4	-19.9
1-bromobutane	DH	-107.1	-110.9	-110.1	-12.6	-11.7	-10.9
2-bromopropane	DH	-99.8	-101.1	-100.5	-31.4	-31.4	-30.7
2-bromobutane	DH	-120.6	-124.2	-123.3	-26.2	-23.2	-22.2
2-bromo-2-methylpropane	DH	-131.6	-139.3	-138.2	-25.8	-33.6	-32.5
1,2-dibromoethane	DH	-43.6	-37.6	-37.3	-18.5	-9.1	-8.7
1,2-dibromopropane	DH	-74.8	-81.7	-80.6	-19.6	-21.2	-20.2
bromoethene	DH	79.2	71.9	71.8	81.6	74.2	74.2
3-bromo-1-propene	DH	49.4	41.4	42.3	80.0	74.0	74.9
Mean deviation			5.1	4.5		3.9	3.7

^a kJ/mol. ^b DH, literature cited in ref 8.

TABLE 10. Experimental Enthalpies and Free Energies of Formation^a and Deviations for Miscellaneous Organic Compounds Determined by G3 and G3MP2 Model Chemistries Using the Bond Separation Method

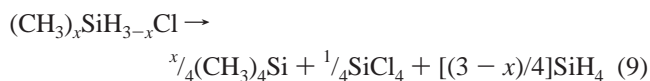
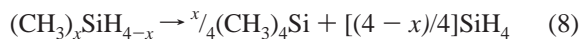
molecule	source ^b	enthalpies of formation			free energies of formation		
		literature	G3	G3MP2	literature	G3	G3MP2
silicon							
dimethyl silane	CIOS	-94.6	-89.5	-88.4	-22.6	-21.5	-21.5
dimethylsilyl chloride	CIOS	-282.0	-278.9	-278.8	-211.5	-211.4	-211.4
trimethylsilane	CIOS	-163.6	-154.4	-152.7	-60.3	-58.6	-58.6
trimethylsilyl chloride	CIOS	-354.0	-352.7	-351.6	-255.8	-254.8	-254.8
mean absolute deviation			4.7	5.7			

^a kJ/mol. ^b CC, ref 2; DH, literature cited in ref 8; GA, values determined by group additivity method in ref 8; CIOS, ref 19.

to those that we applied to the chlorine compounds would afford a result whose deviation would be much larger than what is observed. In contrast, 2-bromobutane would be improved by correction.

The dibromoalkanes and the bromoalkenes have deviations from experiment which are outside the ideal, but within acceptability for both the enthalpies and free energies. These compounds are at lower energy than experiment except for the 1,2-dibromoethane.

Silicon. Finally, we have computed thermodynamic properties of several compounds containing silicon. Our results for the silicon compounds are based on tetramethylsilane rather than CH₃SiH₃ owing to a lack of experimental parameters for the latter. The bond separation reactions are as follows:



The standard state enthalpy for tetramethylsilane given in reference 1 is much lower than most values in the literature. We have used the enthalpy published by Steele⁵⁹ which is identical to the group additivity value obtained by Doncaster and Walsh.⁶⁰ Use of this value gives very good results with the exception of trimethylsilyl chloride.

The results shown in Table 10 indicate that enthalpies can be computed with reasonable accuracy. The two silyl halides are within the ideal range, while the two silanes are less accurate and fall into the acceptable range.

(59) Steele, W. V. *J. Chem. Thermodyn.* **1983**, *15*, 595.

(60) Doncaster, A. M.; Walsh, R. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 707.

Conclusions

Accurate enthalpies and free energies of formation computed using isodesmic bond separation reactions can be obtained for the common families of organic compounds using the G3 methods (G3/G3MP2 or G3B3/G3MP2B3). In the case of secondary and tertiary amines, it is necessary to use semi-homodesmotic reactions in which the degree of nitrogen substitution is maintained on both sides of the reaction arrow. Within these constraints, the four classes of nitrogen compounds examined: amines, hydrazines, nitriles, and amides give excellent results. Several classes of oxygen containing compounds have also been examined. These include the alcohols, ethers, peroxides, aldehydes, ketones, and carboxylic functional groups. In the case of ethers, the data that we have reported was calculated using a semi-homodesmotic reaction, although the improvement is not as dramatic as seen for the secondary and tertiary amines. These classes of compounds are well described by computation with few problem areas. Similar results are found for the sulfur compounds where we also have used the semi-homodesmotic reaction for the sulfides. The only problem in this group of compounds was the disulfides, where there may be a systematic error due to the experimental value for the dihydrogen disulfide that was used in the bond separation reactions. The halogens have more problems; however, we have shown that in some cases the discrepancies may be a result of errors in the experimental values reported in the literature.

The free energies of these compounds are also accurately determined although we have seen that the errors become larger as the length of the carbon chain increases. Correction of these free energies to compensate for the presence of higher energy conformers that have significant populations at 298 K significantly improves the overall mean deviations. As we described in our previous paper, a constant value of 1.2 kJ/mol is

subtracted for each carbon–carbon bond whose rotation affords a different conformer. Bonds to quaternary carbon atoms and those bonds between tertiary carbon atoms separated by one or two bonds are not counted. For the families of compounds that we have examined, the nature of the correction will depend upon the heteroatom. When nitrogen is present, the nitrogen–carbon bond is considered to be equivalent to a carbon–carbon bond with 1.2 kJ/mol subtracted if rotation affords a new conformer. In contrast, a value of 0.5 kJ/mol is applied when a similar carbon–sulfur bond is present. For alcohols and chlorine containing compounds, we subtract an initial 2.5 kJ/mol and an additional 1.2 kJ/mol for each rotatable carbon–carbon bond. For the latter group, this works well with compounds having chlorine at the terminus of the chain. There are insufficient examples of compounds with a chlorine atom on a carbon other than the terminus of the chain to be able to say with certainty that correction on the same basis gives good results and there is some evidence that it does not. There is also insufficient data for aliphatic fluorine compounds to determine whether the free energies need correction or not. Finally bonds adjacent to the carbonyl group are treated as normal carbon–carbon bonds except in the case of the ketones, for which it is not counted. We would have preferred a simpler system where there was more uniformity between the classes of compounds, but this was not to be.

We have defined our deviations as the difference between experiment and computation. It is clear from several examples where we have critically examined the experimental energies that responsibility for a large deviation may not always be lie with the computation. There is a tendency in the literature to look for some patch that will harmonize the literature and

computational results. Before doing so, however, it is important to make sure that we are trying to harmonize more than two numbers and this is particularly true when the computational results are for representative samples from a very large group of compounds. Most compounds are members of a family and the relationship of the computational enthalpy and free energy of formation of any given compound to those of its family members is as important as the relationship to the experimental value. No result should be evaluated out of context.

In this paper we have presented over 250 compounds, nearly all of whose enthalpies of formation match those in the literature within 4 kJ/mol. In addition to nearly 200 compounds whose free energies also match the literature within 4 kJ/mol (when corrected for the presence of multiple conformations), we have presented free energies of formation for another 70 compounds for which no previous value has been available.

Acknowledgment. The hospitality of Dr. Timothy Clark, his group, and the facilities of the Computer Chemie Centrum in Erlangen are gratefully acknowledged. The reviewers are also thanked for insightful comments which have made significant improvements to this work.

Supporting Information Available: Full citations for refs 13 and 14, standard state element entropies, experimental and computed energies of inorganic substances used in the computation of the formation energies, and Cartesian coordinates for all compounds reported here and not available from ref 2; G3 and G3MP2 absolute energies for all organic substances computed for this paper (available in a spreadsheet). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO071213A