Estimated Gas-Phase Standard State Enthalpies of Formation for Organic Compounds Using the Gaussian-4 (G4) and W1BD Theoretical Methods

Sierra Rayne*,‡ and Kaya Forest†

Ecologica Research, Penticton, British Columbia, Canada V1Y 1R9, and Department of Chemistry, Okanagan College, Penticton, British Columbia, Canada V2A 8E1

Gas-phase standard state (298.15 K, 1.01325 bar [1 atm]) enthalpies of formation ($\Delta_f H°_{(g)}$) were calculated using the atomization approach for 313 organic compounds with the Gaussian-4 (G4) composite method and for 54 molecules with the W1BD level of theory. The functional group types considered span a range of mono- and polyfunctionalized halogenated, saturated and unsaturated, cyclic and acyclic, and heteroatom (N, O, S) substituted moieties without substantial conformational complexity. Good agreement was found using both computational methods against available experimental data.

Introduction

Improvements in software development, theoretical approaches, and computing power have led to recent widespread advances in computational thermodynamics over the past several decades.[1] These trends come during a period over which experimental thermochemistry has generally received correspondingly less attention. The apparent inverse temporal correlation between interest in theoretical and experimental thermochemistry is unfortunate, as advancements in instrumental methods now allow the determination of molecular properties such as enthalpies of formation to accuracies not previously accessible.[2] Ideally, the intersection of broadly structured and coupled studies into computational and experimental thermochemistry jointly using the best available methods would facilitate ongoing progress in both fields. This is particularly the situation for some "classic" organic compounds, whose theoretical and experimental prominence came in previous eras, and for which reconsiderations with modern technologies are warranted.

The high level Gaussian-*n* ($n \leq 3$) suite of composite methods (G1, G2, and G3 and their derivatives [e.g., G2MP2, G3MP2, G3MP2B3])[3−9] has been widely benchmarked and employed in the thermochemical study of various compounds,[4,10−23] with less emphasis on the latest G4 and G4MP2 versions[24,25] due to their more recent release.[26−31] Similarly, the W1 methods,[32,33] such as W1BD,[34] have also been introduced for high level calculations. Collectively, these levels of theory appear to offer effective chemical accuracy (< 4.2 kJ·mol^{-1} error) when estimating enthalpies of formation for organic compounds using atomization, isodesmic, and homodesmic approaches, particularly where conformational effects are accounted for using correction factors. In the current work, we examine the gas-phase standard state (298.15 K, 1.01325 bar [1 atm]) enthalpy of formation ($\Delta_f H°_{(g)}$) prediction capacity of the G4 and W1BD methods via the atomization approach on a suite of small- to medium-sized organic compounds having diverse mono- and polyfunctionalization. Our focus is on moieties and larger molecules without substantial conformational complexity that are not often included in benchmarking efforts, as well as the use of the G4 level of theory to estimate $\Delta_f H°_{(g)}$ (and optimized gas-phase geometries) for a number of compounds of broad interest in organic chemistry that lack experimental data.

Experimental Section

Compound structures and experimental data were obtained from the online National Institute of Standards and Technology (NIST) Chemistry WebBook (http://webbook.nist.gov/chemistry/).[35] Where applicable, two-dimensional structures from this reference database were converted to three-dimensional geometries using Avogadro v.1.0.1 (http://avogadro.openmolecules.net/). All compounds were subjected to a systematic rotor search which identified the lowest energy MMFF94[36−40] conformation followed by a 500 step geometry optimization using the steepest descent algorithm and a convergence criterion of 10^{-7} within the Avogadro software environment. The resulting geometries were used as inputs for Gaussian-4 (G4)[24] and W1BD[32,34] composite method calculations with Gaussian 09.[41] All molecular enthalpies include zero-point and thermal corrections, and no compounds have imaginary frequencies at the final optimized geometry. Only the lowest energy conformation of each compound was considered. Gabedit v.2.2.12 (http://gabedit.sourceforge.net/) was used for geometry visualization.[42] Brief descriptions of the G4 and W1BD methodologies are provided in the Supporting Information (SI).

Enthalpies of formation were calculated using the atomization approach[43,44] with the following experimental atomic $\Delta_f H°_{(g)}$ (values in kJ·mol^{-1}):[35,45] H, 217.998 ± 0.006; C, 716.68 ± 0.45; N, 472.68 ± 0.40; O, 249.18 ± 0.10; S, 277.17 ± 0.15; F, 79.38 ± 0.30; and Cl, 121.301 ± 0.008. Corresponding atomic enthalpies at the G4 and W1BD levels of theory are as follows (values in hartrees): G4, H (−0.499060), C (−37.831808), N (−54.571306), O (−75.043141), S (−397.977818), F (−99.702622), and Cl (−460.012692); W1BD, H (−0.497634), C (−37.850525), N (−54.608843), O (−75.108897), S (−399.062789), F (−99.809076), and Cl (−461.431267). Optimized geometries, energies at each step of the calculation process, and frequency coordinates for all compounds are provided in the SI. A conversion factor of 1 hartree = 2625.4997 kJ·mol^{-1} was used for all calculations.

* Corresponding author. E-mail: rayne.sierra@gmail.com.
† Okanagan College.
‡ Ecologica Research.

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Table 1. Experimental and G4/W1BD Calculated Gas Phase Standard State (298.15 K, 1.01325 bar) Enthalpies of Formation ($\Delta_f H^\circ_{(g)}$) for Various Small Organic Compounds[a]

	$\Delta_f H^\circ_{(g)}$/(kJ·mol^{-1})				$\Delta_f H^\circ_{(g)}$/(kJ·mol^{-1})		
compound	expt.	G4	W1BD	compound	expt.	G4	W1BD
1-methylcyclopropene	244.0	241.5	235.7	dimethylamine	−19.0 to −23.8	−15.3	−21.0
1,1-dichloroethene	2.0 to 2.2	2.8	−5.1	ethane	−84.7 to −83.8	−82.9	−88.6
1,1-difluoroethene	−344.0 to −325.0	−348.1	−357.2	ethanol	−235.3 to −232.4	−233.1	−240.7
2-methyl-1-propene	−17.9	−15.3	−22.7	ethylene	52.4 to 52.5	52.6	50.0
acetaldehyde	−170.7	−165.3	−168.6	ethylene oxide	−52.6 to −70.2	−53.1	−55.9
acetic acid	−435.4 to −431.9	−428.8	−435.3	fluoroethene	−136.0	−140.7	−147.0
acetone	−218.5 to −216.4	−214.9	−221.2	formaldehyde	−108.6	−111.2	−110.5
acetonitrile	65.9 to 74.0	73.3	73.8	formic acid	−379.2 to −378.3	−377.6	−381.0
acetylene	226.7 to 227.4	229.1	228.3	furan	−27.7 to −34.7	−32.6	−39.6
bicyclo[1.1.0]butane	217.0	224.6	219.3	hydrogen cyanide	135.1	128.5	131.2
carbon dioxide	−393.5	−396.0	−394.6	methane	−74.8 to −73.4	−74.4	−76.4
carbon disulfide	116.9 to 117.1	105.8	114.4	methanethiol	−22.8	−21.6	−28.2
carbon monoxide	−110.5	−113.7	−110.1	methanol	−214.0 to −200.6	−200.3	−205.1
carbonic difluoride	−640.6 ± 5.9 to −638.9	−606.0	−612.3	methylamine	−23.5 to −12.2	−19.3	−24.6
chloroethene	21.0 to 38.1	22.8	16.3	methylenecyclopropane	201.0	193.8	188.6
chloromethane	−85.9 to −81.9	−81.1	−88.3	oxetane	−80.5 ± 0.6	−78.7	−84.9
chlorotrifluoromethane	−739.5 to −699.0	−707.6	−720.9	phosgene	−220.1 to −209.5	−220.7	−226.6
cis-1,2-dichloroethene	−3.0 to 4.3	0.6	−8.6	propene	20.4	21.1	15.6
cis-2-butene	−7.7	−3.6	−12.0	propylene oxide	−94.7 to −117.1	−93.8	−98.9
cyanogen chloride	138.0	129.3	132.7	propyne	185.4	186.2	183.3
cyclobutene	157.0	163.9	155.8	pyrrole	108.3 to 143.2	109.7	102.6
cyclopropane	39.3 to 53.3	55.2	49.3	tetrafluoromethane	−953.4 to −908.8 (−678.0)	−931.7	−944.5
cyclopropanecarbonitrile	180.6 to 182.7	186.3	184.7	*trans*-1,2-dichloroethene	−1.0 to 1.7	3.2	−6.0
cyclopropene	277.0	285.1	280.6	*trans*-2-butene	−10.8	−9.0	−16.9
dichloromethane	−95.7 to −95.1	−92.5	−102.5	trichloromethane	−103.2 to −102.9	−100.4	−110.6
difluoromethane	−452.2 to −450.7	−450.3	−457.5	trifluoromethane	−697.1 to −690.8	−695.2	−705.4
dimethyl sulfoxide	−150.5	−146.7	−157.4	trimethylamine	−23.7 to −30.7	−24.4	−30.4

[a] Experimental values are the lower and upper boundaries of multiple individual data points with likely outlying experimental data given in parentheses. Experimental data taken from ref 35 with full referencing for all individual data points provided in the SI.

Results and Discussion

The gas-phase standard state (298.15 K, 1.01325 bar [1 atm]) enthalpies of formation ($\Delta_f H^\circ_{(g)}$) were initially calculated at both the G4 and W1BD levels of theory for a set of 54 organic compounds also having experimental $\Delta_f H^\circ_{(g)}$ data for comparison (Table 1). The compounds were chosen to span a range of mono- and polyfunctionalized halogenated, saturated and unsaturated, cyclic and acyclic, and heteroatom (N, O, S) substituted moieties without substantial conformational complexity. As previously noted,[44] where conformationally complex compounds have multiple low-energy conformations that can collectively and significantly contribute to the composite $\Delta_f H^\circ_{(g)}$ measured experimentally, computational approaches that only consider the global minimum conformation will underestimate the conformationally weighted $\Delta_f H^\circ_{(g)}$. Thus, omitting conformational analyses during theoretical $\Delta_f H^\circ_{(g)}$ studies can lead to spurious benchmarking conclusions, such as finding apparent excellent agreement with experimental $\Delta_f H^\circ_{(g)}$ when—if low energy conformations were included in the analysis—the computational approach would overestimate the conformationally averaged experimental $\Delta_f H^\circ_{(g)}$ it is being compared to. Similarly, an apparent $\Delta_f H^\circ_{(g)}$ underestimation by a global minimum theoretical treatment may not be a result of any fundamental inaccuracies in the computational method, but rather the failure to fully account for significant enthalpic contributions from other low-lying conformers.

For broader benchmarking efforts on small- and medium-sized organic compounds, such as those presented herein, full conformational studies on each compound are impractical. Instead, data sets having compounds with higher symmetry and/or rigidity potentially reduce errors from a global minimum theoretical treatment. However, rigid molecules are often strained, and these compounds are difficult to synthesize, purify, and accurately determine their experimental $\Delta_f H^\circ_{(g)}$. Consequently, a paradox arises in computational thermodynamics: either conduct expensive full conformational studies for benchmarking investigations of conformationally complex compounds having more reliable experimental $\Delta_f H^\circ_{(g)}$ data, or use global minimum approaches on more symmetrical and rigid molecules likely to have less reliable experimental $\Delta_f H^\circ_{(g)}$ data. In the first case, it is likely that the experimental $\Delta_f H^\circ_{(g)}$ data will be as accurate as the theoretical estimate. In the second case (particularly where non-C/H functional groups are present that can cause difficulties in ensuring complete experimental combustion), the experimental $\Delta_f H^\circ_{(g)}$ data may be less accurate than that obtained theoretically.

For these reasons, it is difficult to present rigorous error metrics (e.g., mean signed deviation [MSD], mean absolute deviation [MAD], root mean squared deviation [rmsd]) for comparison between the experimental and the G4/W1BD calculated $\Delta_f H^\circ_{(g)}$ data. As evident in Table 1, many compounds (e.g., tetrafluoromethane, pyrrole, etc.) contain wide ranges of individual experimental $\Delta_f H^\circ_{(g)}$ reports (up to $\approx$ 50 kJ·mol^{-1} after screening of clear outliers and up to $\approx$ 300 kJ·mol^{-1} including all available data points), and it is not clear which (if any) of the primary data points are accurate. Furthermore, $\Delta_f H^\circ_{(g)}$ assessments in various standard source compendia and reviews do not generally explain how a final single value was obtained. In some cases, unsatisfying methods such as simply averaging all available experimental data points are used. Even simple compounds such as furan, acetonitrile, and methylamine have experimental $\Delta_f H^\circ_{(g)}$ ranges of (7.0, 8.1, and 11.0) kJ·mol^{-1}, respectively, outside the boundaries of experimental accuracy (4.2 kJ·mol^{-1}) and the error bounds given for each data point. However, with few exceptions, the G4 and W1BD estimates are within the ranges of experimental data (or within several kJ·mol^{-1} where only a single data point is available). The W1BD $\Delta_f H^\circ_{(g)}$ are also systematically lower than the G4

Table 2. Experimental and G4 Calculated Gas-Phase Standard State (298.15 K, 1.01325 bar) Enthalpies of Formation ($\Delta_f H^\circ_{(g)}$) for Various Organic Compounds[a]

compound	$\Delta_f H^\circ_{(g)}$/(kJ·mol^{-1}) expt.	G4	compound	$\Delta_f H^\circ_{(g)}$/(kJ·mol^{-1}) expt.	G4
(1α,2α,4α,5α)-tricyclo[3.2.1.0^{2,4}]oct-6-ene	239.0 to 247.0	233.7	bicyclo[4.2.0]octa-1,3,5-triene	199.4	200.9
(*E*)-hexa-1,5-diyne-3-ene	538.1	526.6	butane	−127.1 to −125.6	−123.6
(*Z*)-3-penten-1-yne	258.0	255.0	carbon suboxide	−97.8 to −93.6	−89.9
(*Z*)-hexa-1,5-diyne-3-ene	541.8	527.3	chlorobenzene	54.4	52.4
1-buten-3-yne	295.0	290.3	chlorotrifluoroethene	−564.8 to −505.5	−505.6
1-cyclopropylpenta-1,3-diyne	484.7	481.6	*cis*-2,3,4-hexatriene	265.0	261.0
1-propynylbenzene	268.2	279.5	*cis*-bicyclo[4.3.0]nona-3,7-diene	109.2	113.1
1,1-dimethylcyclopropane	−8.2	−8.8	cyclobutane, 1,2-bis(methylene)-	204.0	211.4
1,1,1-trichloroethane	−145.0 to −142.3	−146.1	cyclopropane, 1,1-diethynyl-	538.5	547.1
1,1,1-trifluoroethane	−749.0 to −748.7	−750.3	cyclopropanone	16.0	20.4
1,2-bis(methylene)cyclobutane	204.0	211.4	cyclopropylacetylene	292.0	297.1
1,2,3-trichlorobenzene	3.8 to 8.2	5.5	cyclopropylbenzene	150.4 to 150.7	160.9
1,2,4-trichlorobenzene	−8.0 to 4.9	−0.1	difluorodichloromethane	−491.6 to −469.0	−492.2
1,3-cyclopentadiene	133.4 to 139.0	137.1	diketene	−190.2	−190.4
1,3-cyclopentadiene, 5-(1-methylethylidene)-	144.0	145.5	dispiro[2.0.2.1]heptane	302.8	312.5
1,3-dioxol-2-one	−418.6	−396.2	fluorotrichloromethane	−290.0 to −268.3	−288.3
1,3,5-triazine	224.7 to 225.9	224.1	fulvene	224.0	216.6
1,3,5-trichlorobenzene	−2.6 to −13.4	−5.8	hexafluorobenzene	−956.0	−949.3
1,3,5-trioxane	−489.5 to −464.0	−468.3	hexane	−167.2 to −167.1	−165.2
1*H*-imidazole	128.0 to 139.3	131.4	isobutane	−134.2 to −135.6	−132.0
1*H*-pyrazole	177.4 to 181.0	177.3	isopentane	−154.5 to −153.7	−150.6
2-butynedinitrile	529.3	530.1	*m*-dichlorobenzene	28.1	22.0
2-methyl-1-buten-3-yne	259.0	254.8	*m*-difluorobenzene	−309.2	−302.9
2-methyl-1*H*-imidazole	89.8 ± 1.1	88.8	neopentane	−168.5 to −166.0	−166.6
2-methylpyridine	(−26.5) 87.7 to 102.0	99.5	norbornan-7-one	−134.0	−142.2
2-norbornene	63.3 to 90.6 (121.0)	82.0	nortricyclene	62.0 to 99.6	71.5
2-propenenitrile	172.6 to 179.7	186.3	*o*-dichlorobenzene	33.0	28.0
2,2-dimethylbutane	−185.6	−182.3	*o*-difluorobenzene	−283.0	−287.1
2,3-bis(methylene)bicyclo[2.2.0]hexane	315.0	307.6	octahydrodicyclopropa[cd,gh]pentalene	180.0	175.8
2,3-diazabicyclo[2.2.1]-hept-2-ene	196.0	205.8	*p*-dichlorobenzene	24.6	22.7
2,3-dihydrothiophene	90.7	82.2	*p*-difluorobenzene	−306.7	−299.6
2,3-dimethylbutane	−177.8	−174.4	pentane	−147.1 to −146.4	−144.3
2,5-norbornadiene	211.7 to 247.6	239.7	phenol	−96.4 to −94.2	−89.4
3-(*cis*-ethylidene)-1-cyclopentene	84.5	86.9	phenylacetylene	306.6	320.1
3-methylene-1,4-cyclohexadiene	150.0	169.4	propiolonitrile	354.0	373.0
3-methylenecyclopentene	115.0	113.5	pyrazine	196.1	205.3
3,4-dimethylenecyclobut-1-ene	336.0	339.7	pyridazine	278.4	279.8
3,6-bis(methylene)-1,4-cyclohexadiene	210.0	222.7	pyridine	(110.1) 140.2 to 140.7	140.8
4-methylene-2-oxetanone	−190.2	−190.4	pyrimidine	195.8 to 195.9	186.8
5,5-dimethyl-1,3-cyclopentadiene	86.6	81.6	quadricyclane	(253.3) 325.0 to 339.1	334.5
6-methylfulvene	185.0	182.1	spiro[2,4]hepta-4,6-diene	238.0	227.5
7-methylenebicyclo[2.2.1]-heptane	60.0	49.1	spiro[cyclopropane(1,5′)bicyclo[2.1.0]pentane]	288.0	282.8
aniline	81.0 to 87.0	89.7	spiropentane	185.1	185.2
antitricyclo[3.2.0.0^{2,4}]hept-6-ene	383.9	374.2	styrene	(−15.1) 131.5 to 151.5	150.3
antitricyclo[3.2.0.0^{2,4}]heptane	235.0	238.7	tetrachloroethene	−24.0 to −12.4	−24.6
antitricyclo[4.1.0.0^{2,4}]heptane	154.0	155.9	tetrachloromethane	−125.0 to −94.0	−98.0
antitricyclo[4.2.0.0^{2,5}]octane	211.0	217.4	tetracyclo[4.1.0.0^{2,4}.0^{3,5}]heptane	370.0	368.1
benzene	79.9 to 82.9	85.6	tetrafluoroethene	−686.0 to −658.6	−670.2
benzyne	440.0 to 490.0	459.6	tetrahydrofuran	−184.2	−178.9
bicyclo[1.1.0]but-1(3)-ene	544.0	567.8	thiophene	115.0 to 116.7 (218.4)	112.7
bicyclo[1.1.0]butane-1-carbonitrile	304.5	352.1	thiophene, 2,5-dihydro-	87.3	84.5
bicyclo[2.1.0]pent-2-ene	333.0	329.6	toluene	48.0 to 50.1	52.6
bicyclo[2.1.0]pentane	158.0	157.8	*trans*-2,3,4-hexatriene	265.0	261.0
bicyclo[2.1.0]pentane-1-carbonitrile	272.0	278.4	*trans*-bicyclo[6.1.0]nona-2,4,6-triene	372.0	344.7
bicyclo[2.1.1]hex-2-ene	251.0	230.3	trichloroethene	−19.1 to −5.9	−14.1
bicyclo[2.2.0]hex-1(4)-ene	304.0	383.1	tricyclo[4.1.0.0^{2,4}]-heptane	149.0	155.9
bicyclo[2.2.0]hexane	125.0	131.7	tricyclo[4.1.0.0^{2,7}]heptane	191.0	196.4
bicyclo[3.2.0]hept-1-ene	167.0	171.9	trifluoroacetonitrile	−496.6 to −460.0	−498.5
bicyclo[3.2.0]hept-1(5)-ene	173.0	184.3	trifluoroethene	−474.0	−495.4
bicyclo[3.2.0]hepta-2,6-diene	264.0	263.1	tris(methylene)cyclopropane	396.0	441.3
bicyclo[3.2.1]octa-2,6-diene	158.0 to 159.0	148.3			

[a] Experimental values are the lower and upper boundaries of multiple individual data points with likely outlying experimental data given in parentheses. Experimental data taken from ref 35 with full referencing for all individual data points provided in the SI.

level of theory, with MSD, MAD, and rmsd values of (−5.3, 6.0, and 6.7) kJ·mol^{-1}, respectively, between the two methods.

Two sets of error metrics against the experimental data were developed. For each compound, the lowest and highest deviations between the theoretical data point and experimental data point(s) were determined, giving $MSD_{best}/MAD_{best}/rmsd_{best}$ and $MSD_{worst}/MAD_{worst}/rmsd_{worst}$. For the G4 calculations on the G4/W1BD common 54 compound data set, the $MSD_{best}/MAD_{best}/rmsd_{best}$ of (−1.1, 3.2, and 5.8) kJ·mol^{-1}, respectively, were obtained, compared to the $MSD_{worst}/MAD_{worst}/rmsd_{worst}$ of (−1.6, 8.2, and 12.2) kJ·mol^{-1}, respectively. At the W1BD level of theory, the $MSD_{best}/MAD_{best}/rmsd_{best}$ of (4.2, 5.6, and 7.1) kJ·mol^{-1}, respectively, were obtained, compared to the $MSD_{worst}/MAD_{worst}/rmsd_{worst}$ of (3.6, 8.9, and 12.9) kJ·mol, respectively. In both cases, the anomalously high experimental $\Delta_f H^\circ_{(g)}$ of −678.0 ± 8.0 kJ·mol^{-1} for tetrafluoromethane was omitted as an outlier.

Because of computational expense, W1BD calculations were not practical for larger compounds that also have experimental $\Delta_f H^\circ_{(g)}$ values. For these additional 121 molecules, only G4 calculations were completed (Table 2). A generally strong

Table 3. G4 Calculated Gas-Phase Standard State (298.15 K, 1.01325 bar) Enthalpies of Formation ($\Delta_f H^\circ_{(g)}$) for Various Organic Compounds Which Lack Experimental $\Delta_f H^\circ_{(g)}$ Data

compound	G4 $\Delta_f H^\circ_{(g)}$ / kJ·mol^{-1}	compound	G4 $\Delta_f H^\circ_{(g)}$ / kJ·mol^{-1}
(1α,2α,5α,6α)-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene	502.6	4-methylpyrazole	148.0
(1α,2β,5β,6α)-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene	475.6	5-(dimethylamino)tetrazole	327.5
(1α,4α,5β)-5-methyl-2-methylenebicyclo[2.1.0]pentane	259.6	5-ethenylidene-1,3-cyclopentadiene	354.1
[1.1.1]-propellane	360.2	5-methyl-1,3-cyclopentadiene	113.1
1-azetine	193.7	5-methyl-3*H*-1,2-dithiole-3-thione	151.5
1-ethynyl-1-(1-propynyl)cyclopropane	507.1	5-methylenebicyclo[2.2.0]hex-2-ene	354.6
1-methyl-1,2-propadienylcyclopropane	236.2	5-methylenebicyclo[2.2.1]hept-2-ene	187.1
1-methyl-1,3-cyclopentadiene	101.1	5,5-dimethylbicyclo[2.1.0]pent-2-ene	264.9
1-methyl-1*H*-imidazole	123.6	6-methyl-1,2,4-triazine	290.9
1-methyl-3-aminopyrazole	165.9	6-methyltricyclo[4.1.0.0^{2,7}]hept-3-ene	273.0
1-methyl-5-aminopyrazole	174.7	7-methylenebicyclo[2.2.1]hepta-2,5-diene	344.0
1-methylaziridine	121.6	7-methylenebicyclo[3.2.0]hept-1-ene	265.7
1-methylcyclobutene	121.1	7-oxabicyclo[2.2.1]heptane	−176.6
1-methylcyclopropanecarbonitrile	152.5	7-thiabicyclo[4.1.0]heptane	130.9
1-methylcyclopropene-3-carbonitrile	378.9	azetidine	101.4
1-methylnorbornadiene	202.8	benzodithiete	242.0
1-methyltricyclo[4.1.0.0^{2,7}]hept-3-ene	275.3	benzvalene	385.9
1-penten-3-yne	250.0	bicyclo[1.1.1]pentane	201.6
1-pyrazoline	181.5	bicyclo[2.1.1]hexane	59.8
1,1-dicyanoethane	225.2	bicyclo[2.2.0]hex-2-ene	261.6
1,1-dimethyl-2-methylenecyclopropane	128.5	bicyclo[2.2.0]hexa-2,5-diene	404.8
1,1′-biaziridine	355.9	bicyclo[2.2.2]octa-2,5,7-triene	296.0
1,2-cyclobutanedione	−166.6	bicyclo[3.2.0]hepta-1,4,6-triene	446.8
1,2-dimethylcyclopropene	199.8	bicyclo[3.3.0]octa-2,6-diene	131.4
1,2,3-butatriene	322.6	bicyclo[4.1.0]hepta-1,3,5-triene	380.3
1,2,3-triazine	400.5	bicyclo[4.2.0]octa-1,3,5,7-tetraene	409.4
1,2,3,4-pentatetraene	448.7	*cis*-1,2-diethynylcyclopropane	544.6
1,2,4-triazine	335.2	cyanoallene	618.7
1,3-bis(methylene)cyclobutane	222.0	cyclobutadiene	430.4
1,3-dimethylbicyclo[1.1.0]butane	154.6	cyclobutane-1,3-dione	−180.2
1,3-pentadiyne	415.0	cycloocta-1,3-dien-6-yne	436.7
1,4-dioxin	−81.1	cycloocta-1,5-dien-3-yne	401.9
1,4-hexadiyne	415.6	cyclopentyl acetylene	169.4
1,5-dihydropentalene	234.8	cyclopropanimine	224.0
1,5-dimethyl-3-exomethylenetricyclo[2.1.0.0]pentane	421.5	cyclopropylidene cyclopropane	337.5
2-(1,1-dimethylethyl)thiirane	−43.8	cyclopropylidenemethanone	108.0
2-aziridinecarbonitrile	269.5	dihydro-2(3*H*)-thiophenthione	65.6
2-methyl-1-penten-3-yne	214.7	dimethylcyanamide	140.7
2-methyl-1-propen-1-one	−86.5	dithio-*p*-benzoquinone	306.8
2-methyl-1,3-dithiacyclopentane	−4.5	endo-2-methylene-5-methylbicyclo[2.1.0]pentane	221.1
2-methyl-1,5-diazabicyclo[3.1.0]hexane	216.7	ethylidenecyclopropane	163.0
2-methylnorbornadiene	199.7	ethynylcyclobutane	267.7
2-methylthietane	26.2	heptafulvene	266.8
2-oxaspiro[3,3]heptane	−39.5	hex-3-en-1,5-diyne	526.6
2-pyrazoline	176.9	isopropyl isocyanide	28.8
2,2-dimethylthiirane	2.5	methylcyclopropane	26.4
2,4,6-octatriyne	597.2	methylenecyclopropene	388.9
2,5-dihydro-1*H*-pyrrole	117.3	methylmethylenecyclopropane	164.5
2,5-dihydrofuran	−60.9	methyloxirane	−93.8
2(3*H*)-furanone	−248.3	*N*-methylazetidine	86.8
2a,2b,4a,4b-tetrahydrocyclopropa[cd]pentalene	303.7	penta-1,4-diyne	455.4
3-methyl-1,2-dithiolane	−12.3	pentacyclo[3.3.0.0^{2,4}.0^{3,7}.0^{6,8}]octane	445.6
3-methyl-1,2,4-triazine	286.9	pyrrole-2-carbonitrile	237.8
3-methyleneoxetane	22.9	spiro[3.3]hepta-2,5-diene	365.8
3-methylenetetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane	429.1	*syn*-tricyclo[3.2.0.0^{2,4}]heptane	276.6
3-methylthietane	29.1	tetrakis(methylene)cyclobutane	387.1
3,3-dimethylcyclobutene	97.3	thieno[2,3-b]thiophene	214.1
3,3-dimethylcyclopropene	220.7	thieno[3,2-b]thiophene	206.1
3,3-dimethyldiaziridine	148.1	thieno[3,4-b]thiophene	225.0
3,3-dimethyldiazirine	231.3	*trans*-1,2-diethynylcyclopropane	540.7
3,3-dimethylthietane	−9.2	tricyclo[3.1.0.0^{2,6}]hexane	229.3
3(2*H*)-furanone	−205.9	tricyclo[3.1.1.0^{3,6}]heptane	233.9
4-aminopyrimidine	152.7	tricyclo[4.1.0.0^{1,3}]heptane	241.6
4-methyl-1,2-dithiolane	−8.8	tricyclo[4.1.0.0^{2,7}]hept-3-ene	312.5
4-methyl-1,2,3-triazine	354.4	tricyclo[4.1.1.0^{7,8}]oct-2-ene	305.9
4-methyl-1,3-dithiolane	−2.7	tricyclo[4.1.1.0^{7,8}]oct-3-ene	307.1
4-methyl-3*H*-1,2-dithiole-3-thione	149.4	tricyclo[4.1.1.0^{7,8}]octa-2,4-diene	407.8
4-methylene-1,3-dioxolane	−222.9	trimethylthiirane	−28.6
4-methylimidazole	92.6	α-trimethylethylene oxide	−173.6

agreement between the G4 and the experimental $\Delta_f H^\circ_{(g)}$ was observed, yielding the $MSD_{best}/MAD_{best}/rmsd_{best}$ of (−2.1, 6.8, and 12.1) kJ·mol^{-1}, respectively, and the $MSD_{worst}/MAD_{worst}/rmsd_{worst}$ of (−4.3, 14.0, and 27.5) kJ·mol, respectively. Molecular weight scaling errors in $\Delta_f H^\circ_{(g)}$ estimates were not observed using either MSD_{best}/MSD_{worst} (SI, Figure S1a,b) or

MAD_{best}/MAD_{worst} (SI, Figure S2a,b) and the G4 method but are evident at the W1BD level of theory using MSD_{best} (SI, Figure S1c) and MAD_{best}/MAD_{worst} (SI, Figure S2c,d), but not MSD_{worst} (SI, Figure S1d). However, the large degree of scatter and poor quality of fit in the relationship between the minimum and the maximum signed and unsigned $\Delta_f H°_{(g)}$ errors and molecular weight for the W1BD method preclude the development of a reliable correction factor that can be applied to estimated $\Delta_f H°_{(g)}$ values.

Large numbers of conceptually interesting and/or industrially relevant organic compounds also have no experimental $\Delta_f H°_{(g)}$ reports nor any theoretical estimates (particularly at high levels of theory) in the literature. G4 calculations were also completed on 138 of these molecules (Table 3), which is intended to serve as a comparative database for researchers performing future experimental $\Delta_f H°_{(g)}$ determinations, as well as those interested in thermochemical modeling of various processes and fundamental structure−property studies such as molecular strain and geometry relationships.

Conclusions

The gas-phase standard state (298.15 K, 1.01325 bar) enthalpies of formation ($\Delta_f H°_{(g)}$) were calculated at the G4 and W1BD levels of theory for a set of 54 nonconformationally complex small organic compounds, as well as G4 calculations for an additional suite of 121 larger compounds. Good agreement with experimental data was obtained. For compounds having a broad range of experimental $\Delta_f H°_{(g)}$ reports, the high level $\Delta_f H°_{(g)}$ estimates may help resolve which experimental values are more accurate. G4 calculations were also completed on 138 molecules without experimental $\Delta_f H°_{(g)}$ measurements, thereby providing a theoretically rigorous thermochemical and structural database for future thermodynamic studies.

Supporting Information Available:

Optimized geometries, energies at each stage of the optimization process, and frequency coordinates for all compounds investigated, as well as available experimental enthalpies of formation. This material is available free of charge via the Internet at http://pubs.acs.org.

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