

# CCSD(T), W1, and Other Model Chemistry Predictions for Gas-Phase **Deprotonation Reactions**

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Received 27 February 2006; accepted 25 April 2006 Published online 24 July 2006 in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/qua.21105

**ABSTRACT:** A series of CCSD(T) single-point calculations on MP4(SDQ) geometries and the W1 model chemistry method have been used to calculate  $\Delta H^{\circ}$  and  $\Delta G^{\circ}$  values for the deprotonation of 17 gas-phase reactions where the experimental values have reported accuracies within 1 kcal/mol. These values have been compared with previous calculations using the G3 and CBS model chemistries and two DFT methods. The most accurate CCSD(T) method uses the aug-cc-pVQZ basis set. Extrapolation of the aug-ccpVTZ and aug-cc-pVQZ results yields the most accurate agreement with experiment, with a standard deviation of 0.58 kcal/mol for  $\Delta G^{\circ}$  and 0.70 kcal/mol for  $\Delta H^{\circ}$ . Standard deviations from experiment for  $\Delta G^{\circ}$  and  $\Delta H^{\circ}$  for the W1 method are 0.95 and 0.83 kcal/mol, respectively. The G3 and CBS-APNO results are competitive with W1 and are much less expensive. Any of the model chemistry methods or the CCSD(T)/ aug-cc-pVQZ method can serve as a valuable check on the accuracy of experimental data reported in the National Institutes of Standards and Technology (NIST) database. © 2006 Wiley Periodicals, Inc. Int J Quantum Chem 106: 3122-3128, 2006

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Contract grant sponsor: DOD.

Contract grant number: W81XWH-05-1-0441.

Contract grant sponsor: NIH.

Contract grant number: 1R15CA115524-01. Contract grant sponsor: Hamilton College.

Contract grant sponsor: NSF.

Contract grant number: CHE-0457275.

Contract grant sponsor: NSF. Contract grant numbers: CHE-0116435; CHE-0521063.

Contract grant sponsor: ACS PRF. Contract grant number: 37339-B6.

Contract grant sponsor: Research Corporation.

Contract grant number: CC6041.

# Introduction

he ability of modern quantum chemical methods to calculate gas-phase reaction and free energies accurately is essential for a variety of chemical predictions, such as the accurate a priori calculation of gas-phase equilibrium constants. Computed  $\Delta G^{\circ}$  values must be correct to within 1 kcal/mol to achieve chemical accuracy. We have recently evaluated the ability of the Gaussian (Gn) model chemistries [1, 2] and the complete basis set (CBS) model chemistries [3-5] to model gas-phase deprotonation accurately, by examining their performance against 17 reactions in the National Institutes of Standards and Technology (NIST) database [6], where the deprotonation  $\Delta G^{\circ}$  is reported as highly accurate (defined as an experimental error of <1 kcal/mol) [7]. The high computational cost of the model chemistries led us to evaluate a large range of density functional theory methods against the same experimental database [8]. Additionally, a search for the most accurate methods available, combined with a desire to check the experimental data, led us to determine energies with the CCSD(T)/aug-cc-pVnZ model using MP4(SDQ) geometries. In the present work, we report on the performance of CCSD(T) [9] and the W1 model chemistries [10] against this experimental data set [6].

#### Methods

We used the W1 [10] model chemistry and CCSD(T) [9] (coupled cluster with all single and double substitutions along with a quasi-perturbative treatment of connected triple excitations) implemented within Gaussian 03 [11] and Gaussian 98 [12]. The coupled cluster calculations included triple excitations for both the complete fourth-order Møller-Plesset (MP4) and the CCSD(T) energies (E4T keyword). The coupled cluster single-point energy calculations used the augmented correlation consistent polarized n-tuple zeta basis sets (aug-ccpVnZ, n = D, T, Q, 5) of Dunning and coworkers [13-15]. These calculations were performed on geometries obtained using MP4 perturbation theory with single, double, and quadruple substitutions [MP4(SDQ)] [16]. These optimizations, and their corresponding frequency calculations, employed the aug-cc-pVTZ basis set. The frequency calculations ensured that all structures were optimized to a true energetic minima on the potential energy surface (PES), and the unscaled thermochemical corrections were used to obtain the zero-point energy (ZPE), enthalpy, and Gibbs free energy. Furthermore, to estimate the energy at the complete basis set limit, we have performed a series of twopoint extrapolations on the correlation energy [10, 17–19] In this scheme [Eqs. (1)–(3)], an extrapolated value for the correlation contribution to the total energy is obtained using two consecutive correlation energies, x - 1 and x, and is then added to a non-extrapolated Hartree-Fock energy:

$$E_x^{\text{corr}} = E_x^{\text{CCSD(T)}} - E_x^{\text{HF}} \tag{1}$$

$$E_{x-1,x}^{\text{corr}} = \frac{x^3 E_x^{\text{corr}} - (x-1)^3 E_{x-1}^{\text{corr}}}{x^3 - (x-1)^3}$$
 (2)

$$E_{x-1,x} = E_x^{HF} + E_{x-1,x}^{corr}$$
 (3)

Additionally, we corrected for basis set superposition error (BSSE) in the HCl and H2O systems, using the Boys-Bernardi functional counterpoise scheme (fCP) [20].

The W1 model chemistry was developed to be an affordable and accurate method for the determination of thermochemistry [10]. W1 contains one molecule-independent empirical parameter and is based on a series of coupled-cluster calculations, using a variety of robust basis sets. These calculations employ inner shell correlation contributions, scalar relativistic corrections, and two separate twopoint extrapolation schemes for both the valence CCSD energy and valence (*T*) energy contributions.

Obtaining enthalpies and free energies of deprotonation requires the value of H° and G° for the proton. We used the translational energy of 1.5RT combined with PV = RT (H = E + PV) to obtain a value of  $H^{\circ}$  (H<sup>+</sup>) equal to 5/2(RT), or 1.48 kcal/mol. We used the Sackur-Tetrode equation (see Ref. [21]) to obtain the entropy,  $TS(H^+) = 7.76 \text{ kcal/mol}$ at 298K and 1 atm pressure, which gives a value  $(G = H - TS) \text{ for } G^{\circ} (H^{+}) \text{ of } -6.28 \text{ kcal/mol } [22,$ 23]. All values reported in the present work are for a standard state of 1 atm.

## Results

Tables I and II compare the model chemistry results for 17 deprotonation reactions with the experimental results reported in the NIST database [6]. Also presented are previously computed thermochemical results using the CBS-QB3 [5], CBS-APNO [4, 24], and G3 [2] model chemistries [7], as well as the B3P86 and PBE1PBE DFT methods [8]. The standard deviation from experiment,  $\sigma$ , is also included in Tables I and II. The experimental values were taken from the NIST database [6]. Selected systems favored small reported error bars, and recently published data [25-40].

#### **Discussion**

# **MODEL CHEMISTRIES**

The W1 and CBS-APNO model chemistry results have standard deviations of  $\sim$ 1 kcal/mol relative to

**TABLE** 1

Changes in standard free energies (in kcal/mol) for deprotonation of 17 reactants.\*

ΔG°	ΔG° (kcal/mol)		ŏ	3SD(T)/aı	d-cc-bn	VnZ//MP	'4(SDQ)/	CCSD(T)/aug-cc-pVnZ//MP4(SDQ)/aug-cc-pVTZ	/TZ				Model c	Model chemistry		占	DFT <sup>†</sup>
Reactant	Experimental	⊢		a		5		ΔT	0	Q5	O	CBS-QB3	G3	CBS-APNO	W1	B3P86 F	PBE1PBE
C <sub>2</sub> H <sub>2</sub>	$370.29 \pm 0.41^{a}$	371.37	37	370.92	37	371.08	3.	370.45	371	371.18		370.33	370.70	370.28	370.61	371.29	370.64
NH <sub>3</sub>	$396.01 \pm 0.20^{b}$	396.87	39	396.62	š	396.61	ř	396.32	396	396.59		397.40	397.52	396.37	396.40	398.20	398.24
$G_2H_4$	$401.00 \pm 0.50^{\circ}$	400.70	40	400.92	4(	401.05	4	400.93	401	401.12	•	400.37	401.06	400.72	400.56	400.90	400.32
CH <sub>2</sub> O	$386.59 \pm 0.31^{d}$	388.30	38	387.62	38	387.70	33	386.97	387	387.75	.,	388.84	387.66	387.72	387.54	386.63	386.36
HCI	$328.11 \pm 0.20^{f}$	330.40	326.84 32		327.32 33	330.71 32	327.77 32	327.33 327	327.23 332	332.20 32.	327.80	326.78	328.75	N/A	328.00	328.19	327.78
CHNO	$333.60 \pm 0.50^9$	331.49	33	334.28	છે	333.65	છ	332.92	333	333.57		334.49	335.51	335.43	335.15	338.18	337.88
CH⁴	$408.60 \pm 0.79^{h}$	406.48	40	408.99	4(	408.98	4	408.91	406	409.03	•	410.86	410.99	410.45	411.11	410.28	409.62
CH <sub>3</sub> OH	$375.0 \pm 1.1^{i}$	374.00	37	376.75	3.	376.47	3.	376.09	376	376.65	.,	375.52	376.45	375.81	376.61	374.12	374.05
HNO <sub>2</sub>	$333.70 \pm 0.31^{j}$	332.09	33	333.94	33	333.42	છ	332.82	333	333.17		331.67	331.93	332.11	333.17	332.90	332.73
H <sub>2</sub> 0	$383.70 \pm 0.20^{p}$	381.97 382	382.26 38	384.55 383	383.26 38	384.31 38	383.55 38	383.86 383	383.70 384	384.26 383	383.76	385.42	384.75	383.70	384.14	384.77	385.04
CH <sub>3</sub> NH <sub>2</sub>	$395.70 \pm 0.69^{k}$										••	395.95	396.86	395.88	395.92	395.74	395.64
Ξ̈́	$389.20 \pm 0.60^{k}$												388.45	387.86	388.74	387.14	386.84
0.1	$391.71 \pm 0.69^{k}$										.,		391.59	391.19		391.51	391.17
$CH_3CHCH_2$	$383.80 \pm 0.10^{1}$										.,	383.10	383.86	383.14	383.22	380.81	380.07
$C_6H_6$	$392.90 \pm 0.41^{m}$											391.61	392.46	392.05	392.31	394.39	393.86
HNO <sub>3</sub>	$317.81\pm0.20^{n}$											316.21	317.81	317.94	318.51	318.10	317.83
$C_4H_4O(lpha)$	$382.91 \pm 0.20^{\circ}$											382.43	382.85	382.79	382.97	384.59	384.32
$\sigma_{\mathrm{top}}$		1.27	1.17	0.76	0.75	1.17	92.0	0.62	0.63 1	1.59 (	0.80	1.58	1.48	1.20	1.21	2.01	1.89
$\sigma_{ m bottom}$												1.28	0.59	0.74	0.50	1.75	1.94
$\sigma_{ m total}$												1.42	1.17	0.99	0.95	1.84	1.85

\* Values in italics have been corrected for BSSE.

† DFT/aug-cc-pVTZ//DFT/aug-cc/pvTZ.

† DFT/aug-cc-pVTZ//DFT/aug-cc/pvTZ.

† [32]; p[26]; p[26]; p[27]; p[28]; p[26]; p[30]; p[

Changes in standard enthalpies (in kcal/mol) for deprotonation of 17 reactants.\* TABLE II

$^{\circ}$ H $^{\circ}$	ΔH° (kcal/mol)		J	CSD(T)	'aug-cc-	pVnZ//M	P4(SDQ)	CCSD(T)/aug-cc-pVnZ//MP4(SDQ)/aug-cc-pVTZ	pVTZ				Model (	Model chemistry		D	DFT⁺
Reactant	Experimental	⊢		Ø		5		ΔT		Q5		CBS-QB3	G3	CBS-APNO	W1	B3P86 F	PBE1PBE
C,H,	$378.49 \pm 0.20^{a}$	379.38	က	378.93	(,)	379.10	(7)	378.47		379.20		378.33	378.70	378.30	378.58	379.17	378.54
, EHN	$403.39\pm0.10^{b}$	404.38	4	404.14	7	404.13	4	403.84	7	404.11		404.95	405.07	403.91	403.93	405.11	405.14
G <sub>2</sub> H <sub>4</sub>	$409.39 \pm 0.60^{\circ}$	409.09	4	409.30	7	409.43	4	409.31	7	409.50		408.76	409.45	409.12	408.95	409.29	408.71
CH <sub>2</sub> O	$394.50 \pm 0.10^{d}$	396.23	က	395.55	(,)	395.64	(r)	394.90		395.68		397.18	395.63	395.73	395.54	394.63	394.35
HCI	$333.39\pm0.10^{\text{f}}$		332.22 3	334.25 3	332.70	336.09 3	333.15 3	332.71 3	332.61	337.58	333.18	332.15	334.14	N/A	333.37	333.56	333.15
CHNO	$340.01 \pm 0.41^9$		Ó	341.98	(,)	341.98	ന	341.26	.,	341.90		340.88	341.88	341.79	341.55	344.59	344.28
CH⁴	$416.71 \pm 0.69^{h}$		4	417.27	7	417.29	4	417.20	7	417.32		419.13	419.26	418.73	417.91	419.21	418.55
CH <sub>3</sub> OH	$381.7 \pm 1.0^{i}$	383.24	Ø	382.96	ری	383.08	(r)	382.58	.,	383.13		382.69	383.61	382.99	383.09	381.32	381.27
HNO <sub>2</sub>	$340.20 \pm 0.20^{f}$	340.95	Ó	340.44	ری	340.37	(r)	339.84	.,	340.19		339.11	339.39	339.58	340.18	339.97	339.81
H <sub>2</sub> 0	$390.3 \pm 0.20^{p}$	391.15	388.86	0	389.86	390.92	390.15	390.46 3	390.29	390.85	390.35	392.03	391.37	390.31	390.74	391.37	391.64
CH <sub>3</sub> NH <sub>2</sub>	$403.20 \pm 0.79^{k}$											403.38	404.30	403.34	403.37	403.18	403.08
CH <sub>3</sub> NHCH <sub>3</sub>												394.50	395.79	395.19	395.62	394.07	393.78
CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>												398.24	399.03	398.65	398.97	398.97	398.64
CH <sub>3</sub> CHCH <sub>2</sub>	$391.11 \pm 0.31$											391.38	392.02	391.02	390.81	388.56	387.98
$C_eH_e$	$401.70 \pm 0.50^{m}$											400.51	401.27	400.87	401.18	402.63	402.09
HNO3	$324.50 \pm 0.20^{n}$											323.57	324.17	324.31	324.81	325.09	324.84
$C_4H_4O(lpha)$	$391.11 \pm 0.41^{\circ}$											390.66	391.05	390.98	391.18	392.81	392.52
$\sigma_{\mathrm{top}}$		1.50	1.40	1.07	1.04	1.35	1.03	0.91	0.92	1.69	1.03	1.75	1.57	1.32	1.03	2.01	1.89
$\sigma_{ m bottom}$												1.12	0.69	0.68	0.46	1.64	1.80
$\sigma_{ m total}$												1.50	1.27	1.07	0.83	1.81	1.80

\* Values in italics have been corrected for BSSE.

† DFT/aug-cc-pVTZ//DFT/aug-cc/pvTZ.

† DFT/aug-cc-pVTZ//DFT/aug-cc/pvTZ.

† [32]; p[26]; p[26]; p[27]; p[28]; p[26]; p[30]; p[

the experimental values, while the computationally less expensive G3 method yields standard deviations of 1.27 and 1.17 kcal/mol for enthalpy and free energy changes. The CBS-QB3 method, which uses DFT geometries, has standard deviations of 1.5 and 1.4 kcal/mol for enthalpy and free energy changes. W1 is the only method that has a higher standard deviation for free energy changes than enthalpy changes, suggesting that the scaling of the B3LYP/cc-pVTZ frequencies within that method is not optimal for free energies.

A comparison of the model chemistry results to the CCSD(T) results is only possible for the smallest 10 molecules at the top of Table I because of the expense of the coupled clusters calculation scheme. The standard deviations for the CBS-QB3, G3, CBS-APNO, and W1 results of the 10 atom set,  $\sigma_{\text{top}}$ , are 1.8, 1.6, 1.3, and 1.0 for enthalpies and 1.6, 1.5, 1.2, and 1.2 for free energies. This is interesting for two reasons, the first being that the coupled cluster method using a quadruple-zeta basis set is significantly more accurate than the model chemistries. The second, which may be more important for users of these methods, is that the model chemistries are more accurate for the seven largest molecules in this test set. As shown by  $\sigma_{\rm bottom}$ , the G3, CBS-APNO, and W1 model chemistries are better for the larger molecules which are extremely costly to calculate with the CCSD(T) method.

The G3 and CBS-APNO methods model the geometries and energies of hydrogen-bonded water and ion-water clusters quite accurately [41–48], and this deprotonation study adds to the body of evidence that shows the reliability of these two model chemistries. Furthermore, the W1 method, which is computationally more expensive, is also highly accurate. These three model chemistries are more reliable than DFT methods that use the aug-cc-pVTZ basis set for energy calculations [8], and are comparable with the best CCSD(T) results displayed in Tables I and II.

# **COUPLED CLUSTER CALCULATIONS**

Tables I and II show that the CCSD(T)/aug-cc-pVnZ method has the best overall agreement with experiment when n = Q. While collectively the n = 5 results are worse than n = Q, when the HCl outlier is removed the accuracy of the two methods are roughly equivalent. Because the errors associated with the n = T and Q calculations systematically decrease from T to Q, the TQ two-point extrapolation results are in excellent agreement with

experiment. Conversely, there are no systematic changes in the errors between the n = Q and 5 calculations, which is reflected in the extrapolation results. Ignoring the HCl outlier, the calculated values for enthalpy and free energy of reaction are virtually unchanged as the basis is expanded from n = Q to 5. Excluding HCl, recalculation of the standard deviation from experiment for the Q5 extrapolation results in  $\sigma$  falling from 1.59 to 0.86 and from 1.69 to 1.10 for free energy and enthalpy respectively, a nearly equivalent result to the TQ extrapolation. We feel that ignoring the HCl outlier is justifiable, particularly within the context of our extrapolation scheme because the error in the HCl calculated correlation energy increases as the basis set expands, and our two-point extrapolation scheme amplifies this error. The failure of the quintuple-zeta HCl calculation inspired us to perform a very limited set of fCP corrections. We investigated BSSE errors for the aforementioned HCl system, as well as the H<sub>2</sub>O system, which enjoyed favorable agreement with experiment. As shown by the values in italics in Tables I and II, correction for BSSE brings the values for the n = T, Q, and 5 basis sets into better agreement, and the extrapolated TQ and Q5 values are now both in excellent agreement with experiment. Because of the extreme expense of these calculations, we were unable to perform fCP corrections for all ten of the systems studied with coupled cluster theory, and thus we are unable to determine whether this is a fortuitous result or a general trend. However, these results do suggest that even high correlation methods executed with robust basis sets still benefit from fortuitous error cancellation. Feller et al. [49] recently published a careful study of the sources of error for electronic structure calculations on small systems. They used correlation consistent basis sets ranging up to the n = 10 size to show that coupled cluster calculations slowly converge on the total energy as n increases. The raw CCSD(T)/cc-pv10Z energy of the Ne (1S) atom remains 0.6 kcal/mol above the estimated complete basis set limit [49]. Because energy differences converge more rapidly than raw energies, the bond dissociation energy of N2 is converged to 0.5 kcal/mol at the CCSD(T)/cc-pV7Z level [49]. Using simple extrapolation schemes effectively improves the computed properties by an equivalent of increasing the basis set size by three or more cardinal numbers [49]. This suggests that a single-point calculation at the n = 7 or n = 8 level yields results similar to an extrapolated TO or Q5 scheme. Additionally, the CCSD(T) method often

produces results that are in better agreement with full configuration interaction than the more expensive CCSDT method [49]. Thus, we advocate the use of extrapolated TQ values, because of their relatively inexpensive, yet high accuracy predictions. The G3, CBS-APNO, and W1 model chemistry methods appear to be the more efficient route when calculating the thermodynamics of deprotonation for small organic molecules.

Interestingly, the coupled clusters and model chemistry results both consistently disagree with certain experimental results. The NIST values for  $\Delta G^{\circ}$  and  $\Delta H^{\circ}$  have been revised along with the error bars for the experimental deprotonation of methanol since our first use of this data set [7]. The original error bars of 0.6 and 0.4 kcal/mol in the NIST database in 2000 have been revised to 1.1 and 1.0 kcal/mol, and the results here suggest that the error bars are even larger, as the value for  $\Delta G^{\circ}$  should be closer to 376 rather than 375 kcal/mol.

## Conclusion

The model chemistry methods G3, CBS-APNO, and W1 are relatively fast and efficient methods for obtaining deprotonation enthalpies and free energies. Calculations at the CCSD(T)/aug-cc-pVQZ level are very accurate for the 17-molecule test set. Results are worse for a coupled cluster energy calculation using the aug-cc-pV5Z data set, stemming from either better cancellation of errors for the quadruple-zeta basis set or from the effects of BSSE. Any of the model chemistry methods or the CCSD(T)/aug-cc-pVQZ method can serve as a valuable check on the accuracy of experimental data reported in the NIST database.

## **ACKNOWLEDGMENTS**

The authors thank Greg Nizialek and Christy House for preliminary work, and to NSF for support of the MERCURY high-performance computer consortium (http://mercury.chem.hamilton.edu).

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