Comparison of CBS-QB3, CBS-APNO, and G3 Predictions of Gas Phase Deprotonation Data

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The G3, CBS-QB3, and CBS-APNO methods have been used to calculate Δ*H* and Δ*G* values for deprotonation of seventeen gas-phase reactions where the experimental values are reported to be accurate within one kcal/mol. For these reactions, the mean absolute deviation of these three methods from experiment is 0.84 to 1.26 kcal/mol, and the root-mean-square deviation for Δ*G* and Δ*H* is 1.43 and 1.49 kcal/mol for the CBS-QB3 method, 1.06 and 1.14 kcal/mol for the CBS-APNO method, and 1.16 and 1.28 for the G3 method. The high accuracy of these methods makes them reliable for calculating gas-phase deprotonation reactions, and allows them to serve as a valuable check on the accuracy of experimental data reported in the National Institutes of Standards and Technology database.

Introduction

A variety of chemical predictions, such as the accurate a priori calculation of gas-phase equilibrium and rate constants, depend on the ability of modern quantum chemical methods to accurately calculate changes in enthalpy and free energy for gas-phase reactions. To achieve chemical accuracy, computed values of Δ*G* must be correct to within one kcal/mol. We have recently been able to use high level electronic structure methods to calculate accurate pK_a values for carboxylic acids.[1−3] In this previous work, we found that values for deprotonation of carboxylic acids in the gas phase obtained with the G2,[4] G3,[5] CBS-QB3,[6] and CBS-APNO[7,8] methods were within the reported experimental errors.[9] However, the experimental deprotonation data for carboxylic acids was only accurate to ±2 kcal/mol.[9] To better evaluate the ability of the Gaussian model chemistries[4,5] and the Complete Basis Set model chemistries[6−8] to accurately model gas-phase deprotonation, we have measured their performance against seventeen reactions in the NIST database[9] where the deprotonation Δ*G* is reported as highly accurate (which we define as an experimental error of less than 1 kcal/mol). In this paper, we test the performance of the G3, CBS-QB3, and CBS-APNO methods against this stringent data set.

Methods

We used the G3,[5] CBS-QB3,[6] and CBS-APNO[7,8] methods implemented within Gaussian 98.[10] The absence of imaginary frequencies verified that all structures were true minima at their respective levels of theory. We used the translational energy of 1.5*RT* combined with $PV = RT$ ($H = E + PV$) to get a value of $H(\mathrm{H}^+)$ equal to 5/2(*RT*), or 1.48 kcal/mol. We used the Sackur−Tetrode equation[11] to evaluate the entropy, $TS(\mathrm{H}^+) =$ 7.76 kcal/mol at 298 K and 1 atm pressure, which gives a value ($G = H - TS$) for $G(\mathrm{H}^+)$ of −6.28 kcal/mol.[2,12] The geometries of all the stationary points and absolute energies in hartrees of each stationary point at each level of theory are available as Supporting Information. All values reported in this paper are for a standard state of 1 atm.

The G3, CBS-QB3, and CBS-APNO methods are model chemistries developed with the goal of obtaining highly accurate values for thermochemical parameters.[4−8,13−25] In the Complete Basis Set models, a series of calculations are made on a particular geometry, and a complete basis set model chemistry is defined to include corrections for basis set truncation errors. The CBS-QB3 model uses a coupled cluster calculation with triple excitations for the highest level calculation while the CBS-APNO model uses quadratic configuration interaction. Accuracy in structure and energetics requires convergence in basis set size and in the degree of correlation, yet both the expansion of the basis set and increasing the degree of correlation adds significantly to the cost of the calculation. Because the main contribution to structure and energy is obtained at the HF or B3LYP level, the smaller (but critical) corrections to both structure and energy can be determined with less accuracy than at lower levels of theory. The CBS-APNO model makes corrections to the structure, with the final structure computed at the QCISD/6-311G(d,p) level of theory, whereas the CBS-QB3 model does not correct the initial B3LYP structure. Thus, these methods use fairly large basis sets for the structure and first-order Hartree−Fock calculation, medium sized basis sets for the second order correlation correction, and small sized basis sets for higher order correlation corrections. The five step CBS-QB3 series of calculations starts with a geometry optimization at the B3LYP level, followed by a frequency calculation to obtain thermal corrections, zero-point vibrational energy, and entropic information. The next three calculations are single-point calculations (SPCs) at the CCSD(T), MP4SDQ, and MP2 levels. The CBS extrapolation then obtains the final energies. By contrast the CBS-APNO method is a much more expensive, seven step procedure. It starts with a HF/6-311G(d,p) geometry optimization and frequency calculation, followed by a second geometry optimization at the QCISD/6-311G(d,p) level. The QCISD geometry is then used for a series of four SPCs at the QCISD(T), MP2(Full), HF, and MP2 levels, each with different

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TABLE 1: Experimental Values for Deprotonation Reactions in the NIST Database. Numbers with the Smallest Error Bars (in boldface type) Were Used to Determine the Difference between Calculated and Experimental Values. All Values in Kcal/Mol

reaction	ΔGgas (exp 1)	ΔGgas (exp 2)	ΔHgas (exp 1)	ΔHgas (exp 2)	ΔHgas (exp 3)
$NH_3 \rightarrow NH_2^- + H^+$	**396.9± 0.4**[a]	396.1 ± 0.7[b]	**404.30 ± 0.3**[a]	403.60 ± 0.8[b]	
$CH_3NH_2 \rightarrow CH_3NH^- + H^+$	**395.7 ± 0.7**[b]		**403.20 ± 0.8**[b]		
$CH_3NHCH_3 \rightarrow CH_3NCH_3^- + H^+$	**389.2 ± 0.6**[b]		**396.40 ± 0.9**[b]		
$CH_3CH_2NH_2 \rightarrow CH_3CH_2NH^- + H^+$	**391.7 ± 0.7**[b]		**399.3 ± 1.1**[b]		
$CH_4 \rightarrow CH_3^- + H^+$	**408.6 ± 0.9**[c]		**416.70 ± 0.8**[c]		
$CH_3OH \rightarrow CH_3O^- + H^+$	**375.1 ± 0.6**[d]		**381.50 ± 0.4**[d]		
$H_2O \rightarrow OH^- + H^+$	**384.1 ± 0.2**[e]		**390.70 ± 0.1**[e]		
$C_2H_2 \rightarrow C_2H^- + H^+$	**369.8 ± 0.6**[f]	376.8 ± 0.6[g]	378.0 ± 0.7[f]	**379.80 ± 0.5**[d]	385.0 ± 0.7[g]
$C_2H_4 \rightarrow C_2H_3^- + H^+$	**401 ± 0.5**[f]		**409.40 ± 0.6**[f]		
$CH_2O \rightarrow CHO^- + H^+$	**385.6 ± 0.8**[h]		**393.50 ± 0.7**[h]		
$HCl \rightarrow Cl^- + H^+$	328.1 ± 0.2[i]	**328.1 ± 0.1**[j]	**333.40 ± 0.1**[i]		
$CH_3CHCH_2 \rightarrow CH_2CHCH_2^- + H^+$	**383.60 ± 0.5**[k]		**390.20 ± 0.7**[k]		
$CHNO \rightarrow CNO^- + H^+$	**333.6 ± 0.5**[l]		**340.0 ± 0.4**[l]		
$HNO_2 \rightarrow NO_2^- + H^+$	**333.7 ± 0.3**[m]		**340.20 ± 0.2**[m]		
$C_6H_6 \rightarrow C_6H_5^- + H^+$	**392.9 ± 0.4**[n]		**401.70 ± 0.5**[n]	401.80 ± 0.5[o]	
$HNO_3 \rightarrow NO_3^- + H^+$	**317.8 ± 0.2**[p]		**324.50 ± 0.2**[p]	324.50 ± 0.5[q]	
$C_4H_4O \rightarrow C_4H_3O^- + \alpha{-}H^+$ [r]	**382.9 ± 0.2**[s]		**391.10 ± 0.4**[s]		

[a] Ref 26. [b] Ref 27. [c] Ref 29. [d] Ref 31. [e] Ref 34. [f] Ref 35. [g] Ref 37. [h] Ref 39. [i] Ref 42. [j] Ref 43. [k] Ref 44. [l] Ref 46. [m] Ref 51. [n] Ref 52. [o] Ref 60. [p] Ref 55. [q] Ref 61. [r] α-indicates original position relative to oxygen atom. [s] Ref 56.

basis sets. The CBS extrapolation included in the last step then obtains the final energies. The Gaussian-n model chemistries have a similar philosophy and implementation. The G3 method falls between the two CBS methods in terms of computational cost. It starts with a HF/6-31G(d) geometry optimization and a frequency calculation. The third step is an MP2(Full)/6-31G-(d) geometry optimization. The MP2 geometry is then used for a series of four SPCs, at the QCISD(T,E4T)/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p), and MP2(Full)/GTlarge levels. At the end of this seven step procedure the calculated values are used to arrive at the final G3 energies. We have previously provided a fuller description of the details of the Complete Basis Set and Gaussian-n methods,[1,2] and the details of the basis sets and formulas used to obtain the final energies can be found in the original publications.[5−8] These methods have been used to calculate accurate values for enthalpies of formation, atomization energies, ionization potentials, electron affinities, proton affinities, isodesmic reactions, cation-atom reactions, molecule-atom reactions, and to explore activation energy barriers and potential intermediates in chemical reactions.[15−25] In this paper, we compare the ability of these methods to predict ΔG and ΔH for deprotonation reactions in the gas phase, using the most accurate experimental data available.

Results

Table 1 contains all of the values for gas-phase deprotonation for the seventeen reactions reported in the NIST database where an experimental value had an error of less than one kcal/mol.[9] We have included all other reported values for these same seventeen reactions, where the reported uncertainty in the measurement exceeds one kcal/mol, in the table available as Supporting Information.[26−57] Table 2 contains the calculated values for ΔG for 27 reactions. These values include the 17 reactions obtained from the NIST database and reported in Table 1 along with additional reactions that were thought necessary to remove ambiguities in data interpretation or to test the usefulness of the model chemistry methods for discriminating between alternative deprotonation pathways. The CBS-QB3, CBS-APNO, and G3 calculated values in Table 2 are presented in boldface type if they fall within the error bars of one of the experimental values reported in the table in Supporting Information. For the seventeen reactions with error bars less than one kcal/mol, we have 100 calculated values (the CBS-APNO method is not parametrized for chlorine). Of these 100, 62 fall within one of the reported error bars (CBS-QB3: 20, CBS-APNO: 22, G3: 20) of the seventeen reactions in our stringent data set. Table 3 contains the differences between the calculated and experimental values reported in the first two tables, for the seventeen most accurate reactions. For instance, the CBS-QB3 ΔG_{diff} value of −0.50 kcal/mol for the reaction $NH_3 \rightarrow NH_2^- + H^+$ was obtained by subtracting the CBS-QB3 calculated value of 397.40 in Table 2 from the boldface experimental value of 396.9 in Table 1.

Discussion

The agreement between experimental and calculated values for the seventeen deprotonation reactions is generally very good. For the seventeen reactions in Table 3, the mean absolute deviation (MAD) ranges from 0.84 to 1.26 kcal/mol, and the root-mean-square (RMS) deviation ranges from 1.06 to 1.49 kcal/mol. The CBS-APNO values have the best overall agreement with the experimental values that have the smallest error bars, followed by the G3 and CBS-QB3 methods. In the case of acetylene, there are three reported values for ΔH_{gas} that have error bars less than 1 kcal/mol: 378.0 ± 0.7,[35] 379.8 ± 0.5,[31] and 385.0 ± 0.7.[37] Clearly, the value from 1974, 385.0 ± 0.7, based on the flowing after-glow technique,[37] is not as reliable as the two more modern values, based on flowing after-glow[35] and variable-temperature-pulsed-high-pressure mass spectrometry measurements.[31] The table available in Supporting Information contains 34 additional experimental values obtained from the NIST website, with reported errors greater than one kcal/mol, for the 17 reactions in our stringent data set. We have included this information as Supporting Information for experimentalists who can evaluate the reliability of the different experimental methods used to study these deprotonation reactions.

The accuracy of these methods allows one to discriminate between reactions where protons are removed from different parts of the molecule. As Table 2 reveals, deprotonation of CH_3CHCH_2 by two competing reactions, $CH_3CHCH_2 \rightarrow CH_2CHCH_2^- + H^+$, and $CH_3CHCH_2 \rightarrow CH_3CCH_2^- + H^+$, can be easily resolved. Table 2 contains alternative deprotonation pathways for CH_3NH_2, CH_3NHCH_3, $CH_3CH_2NH_2$, CH_3OH, CH_3CHCH_2, $CHOCH_3$, and cyclic C_4H_4O. The G3, CBS-QB3, or CBS-APNO methods are accurate enough, and “black-box”

TABLE 2: Calculated Values (kcal/mol) for 27 Gas-phase Deprotonation Reactions Using the CBS-QB3, CBS-APNO, and G3 Methods. Values in Boldface Are within the Error Bars of the Experimental Values Reported in the Table in Supporting Information[9]

	CBS-QB3		CBS-APNO		G3	
reaction	Δ*G*gas	Δ*H*gas	Δ*G*gas	Δ*H*gas	Δ*G*gas	Δ*H*gas
$NH_3 \rightarrow NH_2^- + H^+$	397.40	404.95	**396.37**	**403.91**	397.52	405.07
$CH_3NH_2 \rightarrow CH_3NH^- + H^+$	**395.95**	**403.38**	**395.88**	**403.34**	396.86	404.30
$CH_3NH_2 \rightarrow CH_2NH_2^- + H^+$	411.44	419.03	411.62	419.20	412.07	419.64
$CH_3NHCH_3 \rightarrow CH_3NCH_3^- + H^+$	387.19	394.50	387.86	395.19	388.45	**395.79**
$CH_3NHCH_3 \rightarrow CH_2NHCH_3^- + H^+$	407.49	415.19	407.93	415.56	408.52	416.13
$CH_3CH_2NH_2 \rightarrow CH_3CH_2NH^- + H^+$	390.79	**398.24**	**391.19**	**398.65**	**391.59**	**399.03**
$CH_3CH_2NH_2 \rightarrow CH_3CHNH_2^- + H^+$	409.01	416.58	409.83	417.50	410.21	417.81
$CH_3CH_2NH_2 \rightarrow CH_2CH_2NH_2^- + H^+$	403.11	411.12	404.00	411.67	404.94	412.55
$CH_4 \rightarrow CH_3^- + H^+$	**410.86**	**419.13**	**410.45**	**418.73**	**410.99**	**419.26**
$CH_3OH \rightarrow CH_3O^- + H^+$	**375.52**	**382.69**	**375.81**	**382.99**	**376.45**	383.61
$CH_3OH \rightarrow CH_2OH^- + H^+$	410.35	417.92	410.43	417.98	410.78	418.32
$H_2O \rightarrow OH^- + H^+$	385.42	392.03	383.70	390.31	384.75	391.37
$C_2H_2 \rightarrow C_2H^- + H^+$	**370.33**	**378.33**	**370.28**	**378.30**	**370.70**	**378.70**
$C_2H_4 \rightarrow C_2H_3^- + H^+$	**400.37**	**408.76**	**400.72**	**409.12**	**401.06**	**409.45**
$CH_2O \rightarrow CHO^- + H^+$	388.84	397.18	387.72	395.73	387.66	395.63
$HCl \rightarrow Cl^- + H^+$	**326.78**	**332.15**	N/A	N/A	**328.75**	**334.14**
$CH_3CHCH_2 \rightarrow CH_2CHCH_2^- + H^+$	**383.10**	**391.38**	**383.14**	**391.02**	**383.86**	**392.02**
$CH_3CHCH_2 \rightarrow CH_3CCH_2^- + H^+$	398.30	405.85	398.90	406.50	399.41	406.98
$CH_3CHCH_2 \rightarrow CH_3CHCH^- + H^+$	401.27	408.93	401.55	409.22	402.06	409.70
$CHNO \rightarrow CNO^- + H^+$	334.49	340.88	335.43	341.79	335.51	341.88
$CHOCH_3 \rightarrow CHOCH_2^- + H^+$	360.25	367.31	360.33	367.33	360.52	367.47
$CHOCH_3 \rightarrow COCH_3^- + H^+$	385.0	393.78	385.87	393.96	386.53	394.57
$HNO_2 \rightarrow NO_2^- + H^+$	331.67	339.11	332.11	339.58	331.93	339.39
$C_6H_6 \rightarrow C_6H_5^- + H^+$	**391.61**	**400.51**	**392.05**	**400.87**	**392.46**	**401.27**
$HNO_3 \rightarrow NO_3^- + H^+$	316.21	**323.57**	**317.94**	**324.31**	**317.81**	**324.17**
$C_4H_4O \rightarrow C_4H_3O^- + \beta{-}H^+$[a]	386.81	395.00	387.69	395.85	387.51	395.68
$C_4H_4O \rightarrow C_4H_3O^- + \alpha{-}H^+$[a]	**382.43**	**390.66**	**382.79**	**390.98**	**382.85**	**391.05**

[a] α- and β-indicate original position relative to oxygen atom.

TABLE 3: Comparison of Calculated and Experimental Values for Gas Phase Deprotonation Reactions for the 17 Reactions in the NIST Database with an Experimental Error Bar of Less than 1 Kcal/Mol.[9] The Experimental Values Are in Boldface Type in Table 1. Differences Reported in Kcal/Mol, with the Computed Values Subtracted from the Experimental Value with the Smallest Error Bar

	CBS-QB3		CBS-APNO		G3	
reaction	ΔG_{diff}	ΔH_{diff}	ΔG_{diff}	ΔH_{diff}	ΔG_{diff}	ΔH_{diff}
$NH_3 \rightarrow NH_2^- + H^+$	−0.50	−0.65	0.53	0.39	−0.62	−0.77
$CH_3NH_2 \rightarrow CH_3NH^- + H^+$	−0.25	−0.18	−0.18	−0.14	−1.16	−1.10
$CH_3NHCH_3 \rightarrow CH_3NCH_3^- + H^+$	2.01	1.90	1.34	1.21	0.75	0.61
$CH_3CH_2NH_2 \rightarrow CH_3CH_2NH^- + H^+$	0.91	1.06	0.51	0.65	0.11	0.27
$CH_4 \rightarrow CH_3^- + H^+$	−2.26	−2.43	−1.85	−2.03	−2.39	−2.56
$CH_3OH \rightarrow CH_3O^- + H^+$	−0.42	−1.19	−0.71	−1.49	−1.35	−2.11
$H_2O \rightarrow OH^- + H^+$	−1.32	−1.33	0.40	0.39	−0.65	−0.67
$C_2H_2 \rightarrow C_2H^- + H^+$	−0.53	1.47	−0.48	1.50	−0.90	1.10
$C_2H_4 \rightarrow C_2H_3^- + H^+$	0.63	0.64	0.28	0.28	−0.06	−0.05
$CH_2O \rightarrow CHO^- + H^+$	−3.24	−3.68	−2.12	−2.23	−2.06	−2.13
$HCl \rightarrow Cl^- + H^+$	1.32	1.25	N/A	N/A	−0.65	−0.74
$CH_3CHCH_2 \rightarrow CH_2CHCH_2^- + H^+$	0.50	−1.18	0.46	−0.82	−0.26	−1.82
$CHNO \rightarrow CNO^- + H^+$	−0.89	−0.88	−1.83	−1.79	−1.91	−1.88
$HNO_2 \rightarrow NO_2^- + H^+$	2.03	1.09	1.59	0.62	1.77	0.81
$C_6H_6 \rightarrow C_6H_5^- + H^+$	1.29	1.19	0.85	0.83	0.44	0.43
$HNO_3 \rightarrow NO_3^- + H^+$	1.59	0.93	−0.14	0.19	−0.01	0.33
$C_4H_4O \rightarrow C_4H_3O^- + \alpha{-}H^+$	0.47	0.44	0.11	0.12	0.05	0.05
Mean Absolute Deviation	1.19	1.26	0.84	0.92	0.89	1.03
RMS deviation	1.43	1.49	1.06	1.14	1.16	1.28

enough, to be used by experimentalists to assist in discriminating between alternative deprotonation reactions in their work.

Earlier calculations on the deprotonation of HNO_3 agree with ours, as Koppel et al.[58] have previously used the G2 method to study the proton affinities of superacids, and they reported a Δ*H* value of 323.8 kcal/mol and a Δ*G* value of 317.4 kcal/mol. These numbers are within 0.4 kcal/mol of the G3 values. Ma et al.[59] have recently used the G3 method to calculate heats of formation, ionization energies, proton affinities, and acidities of hydrochlorofluoromethanes. They found good agreement with most of the experimental data, and the regions of disagreement revealed areas where a more careful examination of the experimental methodology was warranted. The worst agreement in our data set is for the reaction of $CH_2O \rightarrow CHO^- + H^+$, where the computed values are two RMS deviations more positive than the experimental results.[39] If the CH_2O reaction is excluded from the data set, then the MADs (Δ*G*; Δ*H*) are 1.06; 1.11 for the CBS-QB3 method, 0.75; 0.83 for the CBS-APNO method, and 0.82; 0.96 for the G3 method. Similarly, the RMS deviations (Δ*G*; Δ*H*) are 1.23; 1.23 for the CBS-QB3 method, 0.95; 1.03 for the CBS-APNO method, and 1.08; 1.21 for the G3 method.

Conclusion

The G3,[5] CBS-QB3,[6] and CBS-APNO[7,8] methods have been used to calculate ΔH and ΔG values for deprotonation of seventeen gas-phase reactions where the experimental values are reported to be accurate within one kcal/mol.[9] The mean absolute deviation from experiment is 0.84 to 1.26 kcal/mol for these three methods, and the RMS deviation (ΔG; ΔH) is 1.43 and 1.49 kcal/mol for the CBS-QB3 method, 1.06 and 1.14 kcal/mol for the CBS-APNO method, and 1.16 and 1.28 for the G3 method. The combination of high accuracy and relatively low computational cost makes the CBS-QB3 method the best choice of the three. The high accuracy of all of these methods makes them reliable for calculating deprotonation of gas-phase reactions, and allows them to serve as a valuable check on the accuracy of experimental data reported in the NIST database.[9]

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Supporting Information Available: The geometries of all stationary points and absolute energies in hartrees at each level of theory. A table that contains additional experimental values, where the reported uncertainty exceeds one kcal/mol, for all the reactions reported in this paper. This material is free of charge via the Internet at http://pubs.acs.org.

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