Assigning Absolute Values to Proton Affinities: A Differentiation between Competing Scales

Brian J. Smith[1a,b] **and Leo Radom***[,1a]

Contribution from the Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia, and Biomolecular Research Institute, Parkville, VIC 3052, Australia

Received November 20, 1992

Abstract: Ab initio molecular orbital calculations at the G2 level have been used to obtain absolute values for the proton affinities of a variety of prototypical small molecules. A total of 31 molecules were examined. The results are compared with the current standard proton affinity scale and with more recent revisions of this scale. At the lower end of the proton affinity scale, there is generally good agreement between the theoretical and various experimental proton affinities. At the upper end of the scale, the theoretical proton affinities are closer to the original values. However, it is found that all the results can be substantially reconciled if the currently accepted value of the proton affinity of isobutene, used as an absolute standard in several of the experimental determinations, is adjusted downwards by 10–20 kJ mol^{-1}. The theoretical enthalpies for proton-transfer reactions are consistently within 10 kJ mol^{-1} of directly measured experimental enthalpies.

Introduction

In 1984, Lias et al.[2] compiled a comprehensive collection of pre-1984 determinations of relative proton affinities from numerous laboratories, put these for the first time on an internally consistent scale, and assigned absolute values based on the best data available at that time. The resulting proton affinity scale[2,3] has been accepted as the de facto standard. It has been and continues to be widely used, although it is now 10 years old. At the lower end, this scale is believed to be generally reliable, although revisions for some individual molecules have been suggested.[4] The situation is less secure at the upper end, however, because of a lack of suitable absolute standards. Indeed, Mautner and Sieck[5] have recently suggested significant upward adjustments of the proton affinities for molecules at this end of the scale. Their results are supported by other studies by Szulejko and McMahon[6] and by Bisling et al.[7]

An alternative procedure for obtaining proton affinities is provided by ab initio molecular orbital calculations.[8,9] Recent studies by Pople and co-workers[10] have found that the G2 level of theory yields proton affinities consistently to within 10 kJ mol^{-1} of experimental values. Because there is no reason for theory to be any more or less successful at the upper end compared with the lower end of the proton affinity scale, it appears to offer an attractive means of assessing the conflicting experimental scales. To that end, we have carried out a detailed study of the proton affinities of 31 prototypical molecules spanning a wide range of the proton affinity scale (about 500 kJ mol^{-1}), and the results are reported in this paper.

Method and Results

Standard ab initio molecular orbital calculations[8] at the G2 level of theory[10] were performed using the GAUSSIAN 90 and GAUSSIAN 92 programs.[11,12] G2 theory corresponds effectively to QCISD(T)/6-311+G(3df,2p)//MP2/6-31G(d) calculations with zero-point vibrational and "higher-level" corrections. We note that in calculating proton affinities, the empirical higher-level correction cancels; *the resulting proton affinity is thus purely ab initio*. Apart from the standard G2 basis sets, we have used basis sets for bromine, recommended originally for use in G1 theory[13] as specified elsewhere.[14] G2 calculations normally refer to a temperature of 0 K. However, since proton affities are generally reported at 298 K (taken as indistinguishable from 300 K)[2] or sometimes at 600 K, we have evaluated temperature corrections using the scaled calculated vibrational frequencies. We show in Table I the G2 total energies at 0, 298, and 600 K for a variety of molecules and their protonated forms.[15]

Discussion

1. Comparison of Calculated and Experimental Proton Affinity Scales. We begin by comparing G2 proton affinities at 298 and 600 K with values from the experimental scales of Lias et al. (LBLHLM)[3] and Mautner and Sieck (MS),[5] respectively, as presented in Table II.

---

[1] (a) Australian National University. (b) Biomolecular Research Institute.

[2] Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

[3] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data Suppl.* **1988**, 17.

[4] Adams, N. G.; Smith, D.; Tichy, M.; Javahery, G.; Twiddy, N. D.; Ferguson, E. E. *J. Chem. Phys.* **1989**, *91*, 4037.

[5] Mautner, M.; Sieck, L. W. *J. Am. Chem. Soc.* **1991**, *113*, 4448.

[6] Szulejko, J. E.; McMahon, T. B. *Int. J. Mass Spectrom. Ion Proc.* **1991**, *109*, 279.

[7] Bisling, P. G. E.; Ruhl, E.; Brutschy, B.; Baumgartel, H. *J. Phys. Chem.* **1987**, *91*, 4310.

[8] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John-Wiley: New York, 1986.

[9] For recent high-level theoretical studies of proton affinities, see, for example: (a) Dixon, D. A.; Lias, S. G. In *Molecular Structure and Energetics*; Greenberg, A., Leibman, J. F., Eds.; VCH: New York, 1987; Volume 2, Chapter 7. (b) DeFrees, D. J.; McLean, A. D. *J. Comput. Chem.* **1986**, *7*, 321. (c) Del Bene, J. E.; Shavitt, I. *J. Phys. Chem.* **1990**, *94*, 5514. (d) Komornicki, A.; Dixon, D. A. *J. Chem. Phys.* **1992**, *97*, 1087 and references therein.

[10] Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

[11] Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Melius, C. F.; Baker, J.; Martin, R. L.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. GAUSSIAN 90; Gaussian Inc.: Pittsburgh, PA, 1990.

[12] Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. GAUSSIAN 92; Gaussian Inc.: Pittsburgh, PA, 1992.

[13] Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622. Curtiss, L. A.; Jones, C.; Trucks, G. W.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1990**, *93*, 2537.

[14] McGrath, M. P.; Radom, L. *J. Chem. Phys.* **1991**, *94*, 511.

[15] G2 proton affinity data for methane, ethylene, and propene are taken from Wong, M. W.; Radom, L., to be published.

0002-7863/93/1515-4885$04.00/0

Table I. Calculated G2 Energies (hartrees)[a]

	G2(0 K)	G2(298 K)	G2(600 K)		G2(0 K)	G2(298 K)	G2(600 K)
$(CH_3)_2NH_2^+$	−135.23544	−135.22989	−135.21852	$(CH_3)_2NH$	−134.88280	−134.87737	−134.86661
$CH_3NH_3^+$	−96.00779	−96.00332	−96.99539	CH_3NH_2	−95.66691	−95.66252	−95.65506
NH_4^+	−56.78140	−65.77760	−56.77270	NH_3	−56.45865	−56.45484	−56.45034
$(CH_3)_2SH^+$	−477.68620	−477.68008	−477.66803	$(CH_3)_2S$	−477.37187	−477.36598	−477.35505
CH_3CO^+	−152.68112	−152.67654	−152.66893	CH_2CO	−152.36913	−152.36469	−152.35762
$(CH_3)_3C^+$	−157.18055	−157.17311	−157.15786	$(CH_3)_2CCH_2$	−156.87635	−156.86998	−156.85612
HCS^+	−436.01184	−436.00836	−463.00368	CS	−435.71100	−435.70768	−435.70406
$(CH_3)_2OH^+$	−155.04651	−155.04060	−155.02937	$(CH_3)_2O$	−154.74664	−154.74130	−154.73148
$HNCH^+$	−93.55388	−93.55023	−93.54458	HNC	−93.26210	−93.25832	−93.25336
CH_2CHCNH^+	−170.83083	−170.82536	−170.81458	CH_2CHCN	−170.53396	−170.52883	−170.51947
PH_4^+	−342.97571	−342.97177	−342.96587	PH_3	−342.67904	−342.67520	−342.67015
CH_3CNH^+	−132.81837	−132.81350	−132.80460	CH_3CN	−132.52305	−132.51847	−132.51099
$CH_3SH_2^+$	−438.44199	−438.43724	−438.42886	CH_3SH	−438.14847	−438.14390	−438.13647
CH_3CHOH^+	−153.86799	−153.86288	−153.85356	CH_3CHO	−153.57682	−153.57190	−153.56356
CH_2SH^+	−437.22424	−437.22022	−437.21392	CH_2S	−436.93369	−436.92981	−436.92455
$CH_3OH_2^+$	−115.82022	−115.81555	−115.80761	CH_3OH	−115.53489	−115.53060	−115.52392
$CH_3CHCH_3^+$[b]	−117.92704	−117.92112	−117.90959	CH_3CHCH_2[b]	−117.64509	−117.63998	−117.62984
$HC(OH)_2^+$	−189.79721	−189.79293	−189.78547	$HCOOH$	−189.51647	−189.51233	−189.50583
$HCNH^+$	−93.55388	−93.55023	−93.54458	HCN	−93.28489	−93.28142	−93.27691
CH_2OH^+	−114.60776	−114.60387	−114.59829	CH_2O	−114.33893	−114.33512	−114.33036
H_3S^+	−399.19796	−399.19413	−399.18929	H_2S	−398.93073	−398.92694	−398.92277
H_3O^+	−76.59194	−76.58809	−76.58343	H_2O	−76.33205	−76.32827	−76.32429
$HSCS^+$	−833.79160	−833.78684	−833.77992	CS_2	−833.53355	−833.52948	−833.52361
$CH_3CH_2^+$[b]	−78.67361	−78.66931	−78.66171	CH_2CH_2[b]	−78.41593	−78.41193	−78.40534
HCO^+	−113.40110	−113.39768	−113.39329	CO	−113.17749	−113.17419	−113.17079
H_2Br^+	−2573.39314	−2573.38934	−2573.38507	HBr	−2573.17185	−2573.16855	−2573.16517
H_2Cl^+	−460.55213	−460.54836	−460.54421	HCl	−460.34017	−460.33686	−460.33351
CH_5^+[b]	−40.61484	−40.61032	−40.60381	CH_4[b]	−40.41088	−40.40706	−40.40207
$HOCO^+$	−188.56500	−188.56080	−188.55478	CO_2	−188.36131	−188.35774	−188.35283
HNN^+	−109.57858	−109.57507	−109.57047	N_2	−109.39261	−109.38931	−109.38593
H_2F^+	−100.53248	−100.52869	−100.52462	HF	−100.35001	−100.34671	−100.34336
H_3^+	−1.32412	−1.32034	−1.31647	H_2	−1.16636	−1.16306	−1.15971

[a] Calculated total energies for H^+ are G2(298 K) = 0.00236 hartree and G2(600 K) = 0.00475 hartree. [b] From ref 15.

Table II. Calculated (G2)[a] and Experimental[b,c] Proton Affinities (kJ mol^{-1})

	PA_0 G2[a]	PA_{298} G2[a]	PA_{298} LBLHLM[b]	diff[d]	PA_{600} G2[a]	PA_{600} MS[c]	diff[e]
$(CH_3)_2NH_2^+ \rightarrow (CH_3)_2NH + H^+$	925.9	931.7	923	8.7	936.4	953	−16.6
$CH_3NH_3^+ \rightarrow CH_3NH_2 + H^+$	895.0	901.0	896	5.0	906.0	919	−13.0
$NH_4^+ \rightarrow NH_3 + H^+$	847.4[f]	853.6	854	−0.4	858.8	872	−13.2
$(CH_3)_2SH^+ \rightarrow (CH_3)_2S + H^+$	825.3	830.9	839	−8.1	834.2	847	−12.8
$CH_3CO^+ \rightarrow CH_2CO + H^+$	819.1	825.0	828	−3.0	829.8		
$(CH_3)_3C^+ \rightarrow (CH_3)_2CCH_2 + H^+$	798.7	802.1	820	−17.9	804.7	820	−15.3
$HCS^+ \rightarrow CS + H^+$	789.9	795.6	787	8.6	799.1		
$(CH_3)_2OH^+ \rightarrow (CH_3)_2O + H^+$	787.3	792.0	804	−12.0	794.6	805	−10.4
$CH_2CHCNH^+ \rightarrow CH_2CHCN + H^+$	779.4	784.7	794	−9.3	787.3	792	−4.7
$PH_4^+ \rightarrow PH_3 + H^+$	778.9[f]	784.8	789	−4.2	788.9		
$CH_3CNH^+ \rightarrow CH_3CN + H^+$	775.4	780.1	787	−6.9	783.3	789	−5.7
$CH_3SH_2^+ \rightarrow CH_3SH + H^+$	770.6	776.4	784	−7.6	780.1	782	−1.9
$CH_3CHOH^+ \rightarrow CH_3CHO + H^+$	764.5	770.2	781	−10.8	773.9	777	−3.1
$CH_2SH^+ \rightarrow CH_2S + H^+$	762.8	768.7	773	−4.3	772.2		
$CH_3OH_2^+ \rightarrow CH_3OH + H^+$	749.1	754.3	761	−6.7	757.3	761	−3.7
$CH_3CHCH_3^+ \rightarrow CH_3CHCH_2 + H^+$	740.3[g]	744.3[g]	751	−5.7	474.0[g]	750	−3.0
$HC(OH)_2^+ \rightarrow HCOOH + H^+$	737.1	742.9	748	−5.1	746.7		
$HCNH^+ \rightarrow HCN + H^+$	706.2	712.0	717	−5.0	715.2		
$CH_2OH^+ \rightarrow CH_2O + H^+$	705.8	711.8	718	−6.2	715.9		
$H_3S^+ \rightarrow H_2S + H^+$	701.6[f]	707.7	712	−4.3	712.2		
$H_3O^+ \rightarrow H_2O + H^+$	682.3[f]	688.4	697	−0.6	692.8		
$HSCS^+ \rightarrow CS_2 + H^+$	677.5	681.9	688	−6.1	685.4		
$CH_3CH_2^+ \rightarrow CH_2CH_2 + H^+$	676.5[g]	681.9[g]	680	1.9	685.6[g]		
$HCO^+ \rightarrow CO + H^+$	587.1	593.0	594[h]	−1.0	596.6		
$H_2Br^+ \rightarrow HBr + H^+$	581.0	585.9	582[h]	3.9	589.8		
$H_2Cl^+ \rightarrow HCl + H^+$	556.6[f]	561.5	571[h]	−9.5	565.7		
$CH_5^+ \rightarrow CH_4 + H^+$	535.5[g]	539.8[g]	551[h]	−10.2	542.1[g]		
$HOCO^+ \rightarrow CO_2 + H^+$	534.8	539.3	547.5[h]	−7.7	542.7		
$HNN^+ \rightarrow N_2 + H^+$	488.3	493.9	494.5	−0.6	497.0		
$H_2F^+ \rightarrow HF + H^+$	479.1	484.0	489.5	−5.5	488.4		
$H_3^+ \rightarrow H_2 + H^+$	414.2	419.1	423.4	−4.3	424.0		

[a] Calculated from the total energies in Table I. [b] From ref 3. [c] From ref 5. [d] Difference between G2 and LBLHLM (ref 3) values for PA_{298}. [e] Difference between G2 and MS (ref 5) values for PA_{600}. [f] Taken from ref 10. [g] Taken from ref 15. [h] More recent PA_{298} values from ref 4 are 591.6 (CO), 580.7 (HBr), 556.5 (HCl), 543.9 (CH_4), and 537.6 (CO_2), in overall better agreement with G2 theory.

The G2 PA_{298} values span a range of more than 500 kJ mol^{-1} and may be compared with the experimental values of LBLHLM.[3] We find no evidence for any significant variation in the agreement between theory and experiment between the top and bottom of the PA scale. Indeed, the agreement generally is quite remarkable, with the difference between theoretical and experimental proton

Table III. Calculated[a] and Experimental[b] Proton-Transfer Energies (kJ mol^{-1})

	ΔH_{600}		
	G2[a]	MS[b]	diff[c]
$NH_3 + (CH_3)_3C^+ \rightarrow NH_4^+ + (CH_3)_2CCH_2$	−54.1	−53.6	−0.5
$(CH_3)_2S + (CH_3)_3C^+ \rightarrow (CH_3)_2SH^+ + (CH_3)_2CCH_2$	−29.5	−28.5	−1.0
$(CH_3)_2CCH_2 + (CH_3)_2OH^+ \rightarrow (CH_3)_3C^+ + (CH_3)_2O$	−10.1	−14.6	4.5
$(CH_3)_2O + CH_2CHCNH^+ \rightarrow (CH_3)_2OH^+ + CH_2CHCN$	−7.3	−14.2	6.9
$CH_2CHCN + CH_3CNH^+ \rightarrow CH_2CHCNH^+ + CH_3CN$	−3.9	−2.5	−1.4
$CH_3CN + CH_3CHOH^+ \rightarrow CH_3CNH^+ + CH_3CHO$	−9.5	−12.1	2.6
$CH_3CHO + CH_3OH_2^+ \rightarrow CH_3CHOH^+ + CH_3OH$	−16.6	−16.7	0.1
$CH_3OH + CH_3CHCH_3^+ \rightarrow CH_3OH_2^+ + CH_3CHCH_2$	−10.3	−11.3	1.0

[a] Calculated from the total energies in Table I. [b] Taken from ref 5. [c] Difference between G2 and MS values for ΔH_{600}.

Table IV. Calculated[a] and Experimental[b] Proton-Transfer Energies (kJ mol^{-1})

	ΔH_{298}		
	G2[a]	ASTJTF[b]	diff[c]
$CO + H_2Br^+ \rightarrow HCO^+ + HBr$	−6.8	−10.9	4.1
$HCl + CH_5^+ \rightarrow H_2Cl^+ + CH_4$	−21.6	−13.4	−8.2
$CH_4 + HOCO^+ \rightarrow CH_5^+ + CO_2$	−0.5	−6.4	5.9

[a] Calculated from the total energies in Table I. [b] Taken from ref 4. [c] Difference between G2 and ASTJTF values for ΔH_{298}.

Table V. Relative Proton Affinities (kJ mol^{-1})

	$\Delta\Delta H_{600}$[a]		
	G2[c]	MS[d]	diff[b]
$(CH_3)_2NH_2^+ \rightarrow (CH_3)_2NH + H^+$	131.7	133	−1.3
$CH_3NH_3 \rightarrow CH_3NH_2 + H^+$	101.3	99	2.3
$NH_4^+ \rightarrow NH_3 + H^+$	54.1	52	2.1
$(CH_3)_2SH^+ \rightarrow (CH_3)_2S + H^+$	29.5	27	2.5
$(CH_3)_3C^+ \rightarrow (CH_3)_2CCH_2 + H^+$	0.0	0	0
$(CH_3)_2OH^+ \rightarrow (CH_3)_2O + H^+$	−10.1	−15	4.9

[a] ΔH_{600} values relative to that for isobutene. [b] Difference between G2 and MS values for $\Delta\Delta H_{600}$. [c] Calculated from the total energies in Table I. [d] Taken from ref 5.

affinities exceeding the G2 target of 10 kJ mol^{-1} in only four cases: isobutene, dimethyl ether, acetaldehyde, and methane. These will be discussed individually below. The G2 values are generally lower than experiment, the mean difference being 4.4 kJ mol^{-1} in this direction. Two notable exceptions are methylamine and dimethylamine for which the G2 PA$_{298}$ values are somewhat higher than experiment. This could support the argument[5-7] that the LBLHLM values in these two cases are too low, although it would not suggest the need for a large adjustment. The mean absolute deviation between theory and experiment for the 31 comparisons is 6.2 kJ mol^{-1}.

The G2 PA$_{600}$ values may be compared with the experimental results of MS.[5] In this case we observe good agreement between theory and experiment at the lower end of the PA scale but significant discrepancies at the higher end, i.e. for dimethyl ether and stronger bases.

The discrepancies between theory and experiment thus involve four molecules scattered through the LBLHLM scale for PA$_{298}$ values and all the molecules at the upper end of the MS PA$_{600}$ scale.

2. Other Relevant Comparisons. Before attempting to examine the discrepancies in detail, it is useful to make a number of additional comparisons.

Firstly we note that MS have directly determined ΔH_{600} for a number of proton-transfer reactions for which we can make comparisons with G2 results (Table III). There is uniformly good agreement between theory and experiment, including reactions involving the "problem" molecules above. We will return to these shortly. The mean absolute error is 2.3 kJ mol^{-1} and the maximum error is 6.9 kJ mol^{-1}. Szulejko and McMahon (SM)[6] have also recently examined the first reaction in Table III, i.e. the proton-transfer reaction between ammonia and the *tert*-butyl cation, and find a value for ΔH_{500} of −50.2 kJ mol^{-1} which is close to the G2 ΔH_{500} of −53.6 kJ mol^{-1}.

Next we note that Adams et al. (ASTJTF)[4] report ΔH_{298} values for three additional proton-transfer reactions for which comparisons with G2 theory are possible (Table IV). The mean absolute error is somewhat higher but is still quite satisfactory at 6.1 kJ mol^{-1}.

Further, we note that very high level ab initio calculations of the proton affinities of four of the members of our set (CO, CH_4, CO_2, and N_2) have recently been reported by Komornicki and Dixon.[9d] Their calculated proton affinities (593.3, 542.2, 541.0, and 493.3 kJ mol^{-1}, respectively) show an average deviation from the G2 values (PA$_{298}$, Table II) of 1.1 kJ mol^{-1} and a maximum deviation of just 2.4 kJ mol^{-1}.

Finally, we note that the MS PA scale[5] was derived using the PA of isobutene as an absolute standard. This was also the absolute standard in the analysis of SM.[6] We can examine the effect of removal of this absolute standard by evaluating the theoretical and experimental proton affinities at the upper end of the scale *relative to isobutene*. The resulting values (Table V) are all in very good agreement!

3. A Rationalization of the Discrepancies. The results in Tables II–V may be summarized as follows: (a) all but four of the G2 PA$_{298}$ values are within 10 kJ mol^{-1} of the LBLHLM values; (b) the G2 proton-transfer enthalpies are all within 10 kJ mol^{-1} of the *directly measured* experimental proton-transfer enthalpies of MS and ASTJTF; (c) the G2 proton affinities are in close agreement with other recent high-level theoretical results; and (d) the theoretical and experimental *relative* PA$_{600}$ values for molecules at the upper end of the MS scale all agree to within 10 kJ mol^{-1}. These results strongly suggest that G2 theory is capable of reliably predicting proton affinities and that this capability extends across the full proton affinity scale. We may thus use the G2 results with some confidence in attempting to explain the discrepancies between the G2, LBLHLM, and MS scales of proton affinities.

The results of Table V indicate that if the absolute proton affinity of isobutene is lowered by about 15 kJ mol^{-1} from the assumed value, i.e. if PA$_{600}$ = 805 kJ mol^{-1}, and the MS proton affinities at the upper end of the scale are adjusted by this amount, the theoretical and experimental proton affinities for all the molecules of the MS scale would be in close agreement. The largest difference would be less than 5 kJ mol^{-1}. Thus with this single change for the absolute standard, isobutene, the discrepancies between the G2 and MS proton affinities at the upper end of the scale would be removed.

If the MS scale is adjusted, as just described, the difference between the MS and LBLHLM scales would also be reduced significantly, bringing most of the pairs of values to within experimental error of one another. We note in this connection that there is an inherent difference between PA$_{298}$ and PA$_{600}$ values of about 2–5 kJ mol^{-1} that needs to be taken into account. Interestingly, the G2 proton affinities at the upper end of the scale lie between the LBLHLM and the adjusted MS values. On this basis the former may be deduced to be slightly too low and the latter slightly too high.

The rationalization above requires no adjustment at the lower end of the MS scale. Given that a single absolute standard, isobutene, was used for the whole scale, it is not clear why this should be valid. An alternative scenario would be based on the PA_{600} value for isobutene being lowered by 10 kJ mol^{-1} rather than 15 kJ mol^{-1} and with this reduction applied to the whole of the MS scale. This would result in all the MS values agreeing with the G2 predictions to within 10 kJ mol^{-1}, those at the upper end being somewhat higher than the theoretical values and those at the lower end being somewhat lower. The mean absolute deviation would be 5.0 kJ mol^{-1}. A comparison of PA_{298} values obtained on this basis for all the molecules common to the G2, LBLHLM, and MS scales is presented in Table VI. The MS values have been corrected to 298 K for this comparison. The agreement at the upper end of the scale is substantially improved but that at the lower end is made somewhat worse. Again we note that the G2 values generally lie between the LBLHLM and MS values.

We turn now to the four discrepancies between the G2 and LBLHLM scales. The first of these is isobutene, for which we have argued that the standard PA_{600} value appears to be about 10–15 kJ mol^{-1} too high. The equivalent lowering of PA_{298} would be about 13–18 kJ mol^{-1} (to 802–807 kJ mol^{-1}), and this would lead to good agreement between the G2 and LBLHLM values. We note that the relative proton affinity of isobutene and propene has been determined[16] as 55.2 kJ mol^{-1}, quite close to the G2 PA_{298} value of 57.8 kJ mol^{-1}.

Our G2 result suggests that the LBLHLM value for the PA_{298} of dimethyl ether is somewhat too high. The theoretical prediction for dimethyl ether is supported by the satisfactory agreement between the theoretical and directly measured experimental relative proton affinities of dimethyl ether and isobutene (Table III).

Again, the good agreement between the G2 theoretical prediction and the direct measurement of the relative proton affinities of acetaldehyde and methanol (Table III) lends confidence to the theoretical prediction of PA_{298} for acetaldehyde and suggests that the LBLHLM value is slightly too high.

The final discrepancy between G2 theory and the LBLHLM compendium occurs for CH_4. Here we note that the more recent experimental PA value of ASTJTF is 543.9 kJ mol^{-1}. Our G2 result (539.8 kJ mol^{-1}) and other recent high-level theoretical results (541.4, 541.0 kJ mol^{-1})[9b,d] support this revised value.

4. The Proton Affinity of Isobutene and the Heat of Formation of the *tert*-Butyl Cation. The G2 proton affinity of isobutene (PA_{298} = 802 kJ mol^{-1}) is at variance with the current standard value by 18 kJ mol^{-1}. This discrepancy could in principle arise from a discrepancy in the heat of formation for isobutene or for the *tert*-butyl cation. We have therefore calculated each of these separately. The G2 ΔH_{f298} value for isobutene is −14.2 kJ mol^{-1}, in close agreement with the experimental value of −16.9 kJ mol^{-1}.[3] On the other hand, the G2 ΔH_{f298} value for the *tert*-butyl cation is 714.4 kJ mol^{-1} compared with the experimental value of 694 kJ mol^{-1}.[3,17] Our G2 results thus suggest that the current experimental ΔH_{f298} value for the *tert*-butyl cation may be too low by about 10–20 kJ mol^{-1} and that this may be the factor that leads to the discrepancy between theoretical and experimental values of PA_{298} for isobutene.

Table VI. Calculated (G2)[a] and Experimental[b,c] Proton Affinities (PA_{298}, kJ mol^{-1})

	LBLHLM[b]	G2[a]	MS[c]
$(CH_3)_2NH_2^+ \rightarrow (CH_3)_2NH + H^+$	923	932	938
$CH_3NH_3^+ \rightarrow CH_3NH_2 + H^+$	896	901	904
$NH_4^+ \rightarrow NH_3 + H^+$	854	854	857
$(CH_3)_2SH^+ \rightarrow (CH_3)_2S + H^+$	839	831	834
$(CH_3)_3C^+ \rightarrow (CH_3)_2CCH_2 + H^+$	807[d]	802	807
$(CH_3)_2OH^+ \rightarrow (CH_3)_2O + H^+$	804	792	792
$CH_2CHCNH^+ \rightarrow CH_2CHCN + H^+$	794	785	779
$CH_3CNH^+ \rightarrow CH_3CN + H^+$	787	780	776
$CH_3SH_2^+ \rightarrow CH_3SH + H^+$	784	776	768
$CH_3CHOH^+ \rightarrow CH_3CHO + H^+$	781	770	763
$CH_3OH_2^+ \rightarrow CH_3OH + H^+$	761	754	748
$CH_3CHCH_3^+ \rightarrow CH_3CHCH_2 + H^+$	751	744	737

[a] Calculated from the total energies in Table I. [b] From ref 3. [c] From ref 5, but with adjustment (by 10 kJ mol^{-1}) to all the PA_{600} values as a result of such a change to the PA_{600} value for the absolute standard isobutene, and with an additional adjustment from 600 K to 298 K. [d] Adjustment for isobutene as described in footnote *c*.

Concluding Remarks

The G2 level of theory is found consistently to reproduce experimental proton affinities and proton-transfer enthalpies to an accuracy of 10 kJ mol^{-1} for a range of bases with proton affinities spanning some 500 kJ mol^{-1}. There are a small number of discrepant cases but the various results can be substantially reconciled if the currently accepted experimental value of the proton affinity of isobutene is lowered by 10–20 kJ mol^{-1}. Our theoretical results are consistent with a slight upward adjustment of the upper end of the LBLHLM proton affinity scale and a somewhat larger downward adjustment of the MS scale, the latter arising because of the lowered proton affinity of isobutene.[18]

Acknowledgment. We thank Dr. Michael Mautner, Dr. Jan Szulejko, and Professor Terry McMahon for bringing to our attention the conflicting proton affinity scales, prior to the publication of refs 5 and 6. We gratefully acknowledge a generous allocation of time on the Fujitsu VP-2200 of the Australian National University Supercomputer Facility.

---

(16) Lias, S. G.; Shold, D. M.; Ausloos, P. *J. Am. Chem. Soc.* **1980**, *102*, 2540.

(17) See also: Traeger, J. C.; McLoughlin, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3647 and references therein.

(18) **Note Added in Proof:** Since submission of this manuscript, we have become aware of two new sets of relevant experimental data: (a) Proton affinities for CH_2CO, $(CH_3)_2C{=}CH_2$, CH_3CHO, $CH_3CH{=}CH_2$, CH_2O, $CH_2{=}CH_2$, CO, and CO_2 have been determined by Traeger (Traeger, J., to be published) from photoionization experiments. There is a discrepancy of 12.6 kJ mol^{-1} with the G2 proton affinity for isobutene but agreement for the remaining molecules is excellent with a maximum difference between theory and experiment of just 4.4 kJ mol^{-1}. (b) Proton affinities for 48 molecules have been determined by Szulejko and McMahon (Szulejko, J. E.; McMahon, T. B., to be published) from variable temperature proton-transfer equilibria measurements. There is uniformly excellent agreement with the G2 results, the mean error for the 15 cases where comparisons are possible being 2.4 kJ mol^{-1} and the maximum error being 7.0 kJ mol^{-1}. Significantly, the value for isobutene coincides exactly with our G2 result. We thank Drs. Traeger and McMahon for bringing these new data to our attention.