Entropies and Free Energies of Protonation and Proton-Transfer Reactions

3 AUTHORS, INCLUDING:

Brian J Smith
La Trobe Institute for Molecular Science, La T…

107 PUBLICATIONS   **3,438** CITATIONS

SEE PROFILE

Entropies and Free Energies of Protonation and Proton-Transfer Reactions

Allan L. L. East,[1a,b] Brian J. Smith,[1a,c] and Leo Radom*,[1a]

Contribution from the the Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia, National Research Council, Ottawa, K1A 0R6, Canada, and Biomolecular Research Institute, Parkville, VIC 3052, Australia

Received March 20, 1997[⊗]

Abstract: Entropies, enthalpies, and free energies for gas-phase protonation and proton-transfer reactions have been calculated and compared with state-of-the-art experimental values. Statistical entropies have been determined by using ab initio molecular parameters and several previously defined models (E1, E2, and E3). The accuracy of the ab initio proton-transfer entropies (ΔS) obtained with the E3 procedure (1 J mol^{-1} K^{-1}) is significantly better than that normally attainable for ΔS values derived from van't Hoff plots of experimental equilibrium data for proton-transfer reactions (5−10 J mol^{-1} K^{-1}). In fact, even the simplest E1 procedure produces proton-transfer entropies that are accurate to about 1−2 J mol^{-1} K^{-1}. The commonly used isoelectronic approach to estimating entropies of gas-phase ions has been tested. Errors associated with this approximation are generally about 1−3 J mol^{-1} K^{-1}, but can increase to 5−10 J mol^{-1} K^{-1} for systems that have low energy torsional or other floppy modes. G2 enthalpies and E3 entropies have been used to obtain free energies (ΔG) for 25 experimentally observed proton-transfer reactions. The ab initio free energies are in very good agreement with experimental values, the mean absolute deviation being 2.2 kJ mol^{-1} and maximum deviation 4.9 kJ mol^{-1}. There is also very good agreement between theory and experiment for the enthalpies of these proton-transfer reactions with a mean absolute deviation and maximum deviation of 2.7 and 8.5 kJ mol^{-1}, respectively. Theoretical proton affinity (ΔH) and gas-phase basicity (ΔG) scales have been constructed on the basis of G2 energies for 39 molecules and corresponding protonated species. There is generally good agreement between theory and experiment. The small deviations that do exist between theoretical and experimental values appear to correlate with the proton affinity magnitude.

Introduction

In recent years, extensive experimental effort (see, for example, refs 2−8) has been directed toward obtaining scales of proton affinities and gas-phase basicities, i.e., enthalpy (ΔH) and free energy (ΔG) changes, respectively, for reactions:

$$AH^+ \rightarrow A + H^+ \tag{1}$$

The two principal experimental procedures for obtaining the quantitative data required for setting up such scales both involve measuring the equilibrium constant (K) for proton-transfer reactions of the type:

$$AH^+ + B \rightleftharpoons A + BH^+ \tag{2}$$

In the first procedure, K is measured *at a single temperature T*, leading to a value of ΔG according to

$$\Delta G = -RT \ln K \tag{3}$$

from which ΔG scales of gas-phase basicities may be constructed. The enthalpy changes required for the proton affinity

scales are then obtained from the ΔG values by using the equation

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

by estimating a value of ΔS. This procedure has the disadvantage that T is not always well-defined experimentally and ΔS is not always easy to estimate, particularly for cations.

In the second procedure, K is measured *at a series of temperatures*. A van't Hoff plot of ln K against $1/T$ then directly yields ΔH from the slope and ΔS from the intercept:

$$\ln K = -\Delta H/RT + \Delta S/R \tag{5}$$

This method has the major advantage of minimizing errors, since random errors in K and T should tend to cancel in a linear fit to the data, and ΔS need no longer be estimated. However, systematic errors in K and/or T may still arise, and the assumptions that ΔH and ΔS are not temperature dependent over the experimental temperature range are still required.

The proton-transfer equilibrium measurements yield *relative* values of the free energy, enthalpy, and entropy changes associated with protonation of individual species. To assign *absolute* values, one or more anchoring values from a separate experiment are required.

An alternative means of obtaining gas-phase thermochemical information is through high-level ab initio molecular orbital calculations. For example, extensive recent studies[9−12] have demonstrated excellent agreement between experimental proton

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1997.

(1) (a) Australian National University. (b) National Research Council of Canada. (c) 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* **1988,** *17,* Suppl. 1.

(4) Adams, N. G.; Smith, D.; Tichy, M.; Javehery, 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. *J. Am. Chem. Soc.* **1993,** *115,* 7839.

(7) (a) Traeger, J. C. *Rapid Commun. Mass Spectrom.* **1996,** *10,* 119. (b) Traeger, J. C. Unpublished results.

(8) Sieck, L. W. To be submitted for publication.

(9) Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1993,** *115,* 4885.

(10) Smith, B. J.; Radom, L. *J. Phys. Chem.* **1995,** *99,* 6468.

(11) Glukhovtsev, M.; Szulejko, J.; McMahon, T. B.; Gauld, J. W.; Scott, A. P.; Smith, B. J.; Pross, A.; Radom, L. *J. Phys. Chem.* **1995,** *98,* 13099.

(12) Smith, B. J.; Radom, L. *Chem. Phys. Lett.* **1994,** *231,* 345.

affinities and theoretical values calculated at the G2 level of theory[13] and some of its more economical variants.[10,14,15] One advantage of the theoretical procedure is that absolute values of the thermodynamic parameters are obtained for the individual species. Potential cumulative errors associated with the anchoring approach used in the experimental studies are thus eliminated.

It is of interest now to carry out a parallel investigation of entropies of protonation and proton-transfer reactions. In this way, the validity of the assumptions made in estimating entropies in the single-temperature procedure above for calculating proton affinities may be evaluated. In addition, the calculated entropies may be compared with the directly measured values obtained from experimental van't Hoff plots in the variable-temperature procedure. The results of such an investigation are reported in the present paper. The entropy results will also allow us to reexamine the extensive experimental proton affinity and gas-phase basicity ladders which have appeared in the last 6 years.[5,6,8]

Theoretical Methods

Standard ab initio molecular orbital calculations[16] were performed at a number of levels of theory, using various versions of the GAUSSIAN[17] and MOLPRO[18] codes. Electronic energies required for the enthalpy and free energy calculations were computed by using G2 theory.[13] G2 theory corresponds effectively to QCISD(T)/6-311+G-(3df,2p) energy calculations on MP2(full)/6-31G(d) optimized geometries together with zero-point vibrational energy and higher level corrections.

In a recent study,[19] we defined three procedures for the statistical calculation of absolute third-law entropies, denoted E1, E2, and E3 in order of increasing sophistication. In the present work, we focus on the best results (E3) but also present a brief comparison with the simpler E1 and E2 models to examine their accuracy. Unless otherwise noted, however, the results in the text refer to E3.

For molecules without internal rotation modes, the E1, E2, and E3 models are identical. They use standard statistical thermodynamic formulae and assume the harmonic oscillator (HO) approximation throughout. All three procedures use geometries optimized at the second-order Møller−Plesset perturbation theory level with the 6-31G-(d) basis set (MP2(fc)/6-31G(d)) and harmonic vibrational frequencies calculated at the Hartree−Fock level with the 6-31G(d) basis set (HF/6-31G(d)) and scaled by 0.8929. Only the most abundant isotopes have been used, and no electronic or nuclear spin effects have been included in the entropy calculations. The frozen-core approximation has been used in all the entropy calculations.

(13) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(14) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.

(15) Curtiss, L. A.; Redfern, P. C.; Smith, B. J.; Radom, L. *J. Chem. Phys.* **1996**, *104*, 5148.

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

(17) (a) 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, 1992. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. GAUSSIAN 94; Gaussian, Inc.: Pittsburgh, 1995.

(18) MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles, with contributions by J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. M. Pitzer, A. J. Stone, P. R. Taylor, and R. Lindh.

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

In the (simplest) E1 procedure, internal rotations are treated either by using the harmonic oscillator approximation if the MP2/6-31G(d) barrier is greater than $1.4RT$ or as a free rotor if the barrier is less than $1.4RT$.[19] This corresponds to a changeover point at about 3.5 kJ mol^{-1} at 298 K or 7.0 kJ mol^{-1} at 600 K. In the E2 and E3 procedures, torsional entropies for species with a single internal rotation are computed by using the hindered rotor tables of Pitzer and co-workers.[20,21] The required rotational potentials are obtained from MP2/6-311+G(2df,p) energy calculations at MP2(fc)/6-31G(d) optimized geometries.

For species with two internal rotations, E2 maintains an independent-mode approach whereas E3 takes into account the coupling of the two modes. In computing E3 entropies in the present work, we use the two-dimensional coupled potential surfaces presented in our previous paper[19] with the scaled partition function of Pitzer and Gwinn.[20]

There were three trimethyl cases encountered in the present study, for which the E3 procedure is not strictly defined. We have approximated the methyl torsions in $(CH_3)_3N^+$ and $(CH_3)_3NH^+$ as harmonic oscillations (as in the E1 procedure) and those of the *tert*-butyl cation $[(CH_3)_3C^+]$ as free rotors (also as in E1 theory, although the moments of inertia in our E3 results were obtained by using the E3 prescription).

Enthalpies (ΔH) were calculated by using the G2 energies and scaled HF/6-31G(d) harmonic vibrational frequencies. Free energies (ΔG) were obtained from the calculated enthalpies and entropies with eq 4. The calculated thermodynamic properties all refer to 1 atm of pressure.

Results and Discussion

Experimental Data Set. Our theoretical results are compared throughout with state-of-the-art experimental data obtained from two sets of recent variable-temperature proton-transfer equilibrium measurements carried out by Mautner and Sieck[5,8] in the NIST laboratories and by Szulejko and McMahon[6] at the University of Waterloo. We note that the original Mautner−Sieck data[5] for species with proton affinities at or below methyl acetate have been superseded by new data from Sieck,[8] and we have used the appropriate replacements in our comparisons. For brevity, the NIST and Waterloo data sets are referred to as MauS/S and SMc, respectively.

Absolute Entropies. Calculated third-law entropies at 1 atm of pressure and three selected temperatures (298, 500, and 600 K) are summarized in Table 1. We can see that protonation typically increases the entropy of a neutral molecule by 2 to 10 J mol^{-1} K^{-1} at room temperature, with greater increments being observed if protonation reduces the rotational symmetry number, introduces a third rotational degree of freedom to a formerly linear species, or creates a new internal rotation. A lowering of the entropy is observed for protonation of amines (except trimethylamine) and phosphine.

The greatest increases in entropy upon protonation in our data set occur for the linear species CO_2, OCS, and CS_2, due to the creation of a third rotational degree of freedom. Protonation of the sulfur sites in these molecules provides a greater increase in entropy than protonation of oxygen sites due to the smaller ∠HSC angles (relative to ∠HOC angles), which produce a larger axial moment of inertia. Although protonation of OCS occurs at the sulfur (vide infra), protonation of CS_2 is still accompanied by a greater increase in entropy due to the greater loss of rotational symmetry in the CS_2 molecule ($D_{\infty h} \rightarrow C_s$) relative to OCS ($C_{\infty v} \rightarrow C_s$). The particularly high entropy of protonation of CS_2 has been previously correctly attributed to rotational effects by Mautner and Field.[22]

The Isoelectronic Approximation. A common rule of thumb for estimating the absolute third-law entropy of a gas-

(20) Pitzer, K. S.; Gwinn, W. D. *J. Chem. Phys.* **1942**, *10*, 428.
(21) Li, J. C. M.; Pitzer, K. S. *J. Phys. Chem.* **1956**, *60*, 466.
(22) Mautner, M.; Field, F. H. *J. Chem. Phys.* **1977**, *66*, 4527.

Table 1. Calculated E3 Third-Law Entropies at 298.15, 500, and 600 K Temperatures (J mol^{-1} K^{-1})[a]

	ΔS^{298}	ΔS^{500}	ΔS^{600}		ΔS^{298}	ΔS^{500}	ΔS^{600}
$(CH_3)_3N$[b]	290.1	347.3	374.0	$(CH_3)_3NH^+$[b]	294.1	354.0	382.2
$(CH_3)_2NH$	273.8	318.4	338.6	$(CH_3)_2NH_2^+$	271.4	317.7	339.1
pyridine	282.5	336.0	361.4	$C_5H_6N^+$	284.8	341.1	368.1
$CH_3CH_2NH_2$	282.9	328.2	348.6	$CH_3CH_2NH_3^+$	277.5	324.7	346.3
CH_3NH_2	242.2	272.5	285.9	$CH_3NH_3^+$	235.6	267.9	282.5
pyrrole	271.0	319.9	342.9	$C_4H_6N^+$	279.8	330.3	354.6
NH_3	192.4	211.7	219.4	NH_4^+	185.9	205.7	214.1
$(CH_3)_2S$	286.3	331.3	350.7	$(CH_3)_2SH^+$	295.0	344.4	366.0
CH_2CO	241.2	271.1	283.4	CH_3CO^+	243.6	275.3	288.8
$(CH_3)_2CO$	295.9	342.7	363.8	$(CH_3)_2COH^+$	304.7	354.8	377.7
$(CH_3)_2CCH_2$	293.4	349.5	374.9	$(CH_3)_3C^+$[b]	309.6	365.2	391.2
CS	210.5	226.4	232.4	HCS^+	213.8	233.8	241.8
CH_3CH_2CN	286.0	331.5	351.6	$CH_3CH_2CNH^+$	291.6	343.1	365.7
$(CH_3)_2O$	267.6	308.1	326.2	$(CH_3)_2OH^+$	284.1	328.9	348.9
PH_3	210.0	231.2	240.1	PH_4^+	203.2	227.7	238.3
C_2H_3CN	273.5	312.3	329.1	$C_2H_3CNH^+$	278.4	323.1	342.4
CH_3OCHO	286.1	325.5	343.0	CH_3OCHOH^+	291.2	334.8	354.3
CH_3CN	242.9	274.1	287.5	CH_3CNH^+	247.2	284.2	300.1
CH_3SH	255.1	285.0	297.8	$CH_3SH_2^+$	258.7	293.0	307.8
HNC	205.2	226.9	235.1	$HCNH^+$	205.3	229.2	239.1
CH_3CHO	264.0	297.1	311.7	CH_3CHOH^+	265.3	302.8	319.5
CH_2S	230.8	253.0	262.2	CH_2SH^+	241.6	267.7	279.0
CH_3OH	239.9	266.3	277.9	$CH_3OH_2^+$	247.2	278.8	292.7
$HCOOH$	248.8	275.8	287.4	$HC(OH)_2^+$	251.5	282.1	295.6
CH_3CHCH_2	266.8	307.6	326.2	$(CH_3)_2CH^+$	277.1	321.4	341.7
HCN	201.3	220.8	228.4	$HCNH^+$	205.3	229.2	239.1
CH_2O	218.7	238.8	247.1	CH_2OH^+	228.3	251.3	261.4
H_2S	205.5	223.8	230.7	H_3S^+	208.9	229.4	237.8
H_2O	188.9	206.5	212.9	H_3O^+	193.6	213.7	221.6
CS_2	237.9	263.4	273.3	$HSCS^+$	269.2	299.2	310.9
C_2H_4	219.1	245.9	258.0	$C_2H_5^+$	231.3	262.0	276.1
OCS	232.1	255.9	265.1	$HSCO^+$	258.8	287.6	298.8
OCS	232.1	255.9	265.1	$HOCS^+$[c]	252.4	280.0	291.0
CO	197.8	213.0	218.5	HCO^+	201.6	220.5	228.0
HBr	198.5	213.6	219.0	H_2Br^+	218.8	237.4	244.5
HCl	186.5	201.6	207.0	H_2Cl^+	205.9	224.1	230.9
CO_2	213.9	235.0	243.4	$HOCO^+$	240.3	266.1	276.4
N_2	191.9	207.0	212.5	HNN^+	202.5	222.4	230.2
HF	173.8	188.8	194.1	H_2F^+	191.1	209.1	215.7
H_2	130.1	145.2	150.5	H_3^+	146.5	163.8	170.0

[a] Entropy values for H$^+$ are 108.8 (298 K), 119.6 (500 K), and 123.4 (600 K) J mol^{-1} K^{-1}. [b] E1 method used for $(CH_3)_3N$, $(CH_3)_3NH^+$, and $(CH_3)_3C^+$. [c] Higher energy product of protonation of neutral species.

Table 2. Comparison of Entropies of Isoelectronic Species (J mol^{-1} K^{-1})

		S^{298}			S^{600}
cation	[neutral]	cation	neutral	difference	diff
HCO^+	[HCN]	201.6	201.3	−0.3	+0.4
HNN^+	[HCN]	202.5	201.3	−1.2	−1.8
H_3O^+	[NH$_3$]	193.6	192.4	−1.2	−2.3
H_3S^+	[PH$_3$]	208.9	210.0	+1.1	+2.2
H_2F^+	[H$_2$O]	191.1	188.9	−2.2	−2.8
H_2Cl^+	[H$_2$S]	205.9	205.5	−0.4	−0.2
$CH_3OH_2^+$	[CH$_3$NH$_2$]	247.2	242.2	−5.0	−6.7
$(CH_3)_2OH^+$	[(CH$_3$)$_2$NH]	284.1	273.8	−10.3	−10.3

phase ion is to assume it is equal to that of the isoelectronic neutral analogue.[6] We are able to explicitly test this approximation here. Among the cations listed in Table 1, there are eight for which we have neutral analogues, and we list these as test cases in Table 2. The first six results suggest that the isoelectronic approximation might be generally reliable to within about 1−3 J mol^{-1} K^{-1} for small species with no internal rotations. For the two systems with internal rotations, the errors are larger (−5.0 J mol^{-1} K^{-1} for $CH_3OH_2^+$ and −10.3 J mol^{-1} K^{-1} for $(CH_3)_2OH^+$ at 298 K). Important contributions to the errors in these cases come not only from the internal rotation(s) (errors of −1.7 and −6.3 J mol^{-1} K^{-1}, respectively) but also from the low-frequency bending modes (errors of −1.9 and −3.0 J mol^{-1} K^{-1}, respectively). This suggests that the isoelectronic

approximation should be used with caution for systems with internal rotations or other high-entropy large-amplitude motions.

Proton-Transfer Entropies. Entropies for 25 proton-transfer reactions were computed at 500 and 600 K by using the results in Table 1, and they are compared with experimental results[5,6,8] in Table 3 and the corresponding Figure 1. The differences between theoretical ΔS^{500} and ΔS^{600} values are quite small (Table 3), indicating that there is little temperature dependence of ΔS values for these reactions, at least over the 100 K temperature interval considered. The mean absolute difference between the theoretical 500 and 600 K ΔS values is 0.5 J mol^{-1} K^{-1}, with a maximum difference of 1.9 J mol^{-1} K^{-1}.

In previous work,[19] we showed that third-law entropies computed by using the E3 procedure should be accurate to within about 1 J mol^{-1} K^{-1}. Figure 1 suggests that the direct experimental entropies are not so accurate, with discrepancies of up to 13 J mol^{-1} K^{-1} when compared with the theoretical values. Indeed, there are discrepancies of up to 5 J mol^{-1} K^{-1} between the ΔS results obtained for the same reaction from the two independent experimental groups. The mean absolute deviation between the Szulejko−McMahon (SMc) and theoretical results is 6.6 J mol^{-1} K^{-1}, with a maximum deviation of 12.6 J mol^{-1} K^{-1} (13 comparisons). The Mautner−Sieck (MauS/S) results are somewhat closer to the theoretical values, with a mean absolute deviation of 4.5 J mol^{-1} K^{-1} and a maximum deviation of 9.6 J mol^{-1} K^{-1} (15 comparisons).

Table 3. Theoretical and Experimental Entropies for Directly Measured Proton-Transfer Reactions (J mol^{-1} K^{-1})^a

	A	B	ΔS^{500} theory	ΔS^{500} SMc^b	ΔS^{600} MauS/S^c	ΔS^{600} theory
1	N_2	CO_2	15.7	13.8		15.3
2	CO	OCS	24.2^d	20.1		24.2^d
3	$(CH_3)_2CCH_2$	NH_3	−21.7	−30.5	−25.9	−21.6
4	CH_3NH_2	$(CH_3)_2NH$	4.1	5.9		4.0
5	CH_3OCHO	$(CH_3)_2CO$	2.8	15.1		2.6
6	NH_3	pyrrole	16.4	9.6	12.6	16.9
7	$(CH_3)_2NH$	$(CH_3)_3N$	7.3		5.0	7.7
8	$(CH_3)_2CCH_2$	$(CH_3)_2S$	−2.7		−8.8	−1.1
9	pyridine	$(CH_3)_3N$	1.6		−3.8	1.5
10	$CH_3CH_2NH_2$	pyridine	8.6		13.0^e	9.0
11	CH_3CH_2CN	$(CH_3)_2CO$	0.6		−2.0	0.0
12	H_2O	H_2S	−1.6	−2.1		−1.5
13	pyrrole	CH_3NH_2	−15.1	−16.3		−15.1
14	CH_3CH_2CN	$(CH_3)_2CCH_2$	4.2		1.5	2.3
15	CH_3CN	CH_3CH_2CN	1.5		−1.0	1.4
16	CH_3CHO	CH_3CN	4.4		−3.0	4.8
17	$(CH_3)_2S$	NH_3	−19.0		−10.9	−20.5
18	CH_3OCHO	CH_3CH_2CN	2.2		−6.0	2.6
19	$(CH_3)_2O$	$(CH_3)_2CCH_2$	−5.0	5.0		−6.4
20	CH_3CHCH_2	CH_3OH	−1.3	−12.6		−0.7
21	H_2O	CS_2	28.5	41.0		28.9
22	CS_2	H_2S	−30.1	−42.7		−30.5
23	$(CH_3)_2CCH_2$	$(CH_3)_2CO$	−3.7	−2.1	−3.1	−2.3
24	$(CH_3)_2NH$	pyridine	5.7		7.5	6.2
25	CH_3CN	CH_3OCHO	−0.7		4.2	−1.2

^{a} Entropies of proton-transfer reactions AH$^+$ + B → A + BH$^+$, written in order of increasingly exothermic free energy changes (cf. Table 7). ^{b} From Szulejko and McMahon (ref 6). ^{c} From Mautner and Sieck (ref 5) and Sieck (ref 8). ^{d} Assumes 100% protonation on the sulfur site of OCS. ^{e} Appears negative in ref 5 due to possible typographical error.
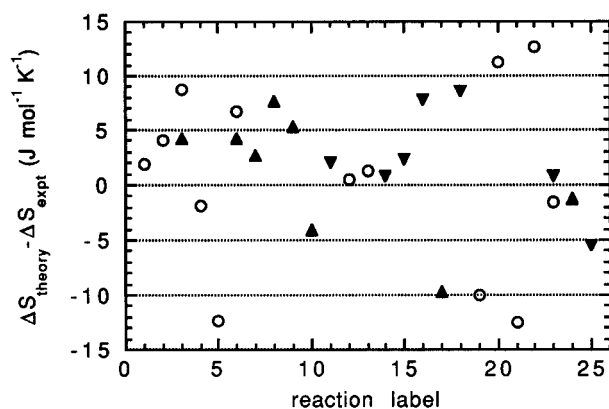

Figure 1. Differences between theoretical and experimental entropies ($\Delta S_{\text{theory}} - \Delta S_{\text{expt}}$) for the 25 proton-transfer reactions of Table 3, listed in order of decreasingly exothermic ΔG (cf. Table 7). Experimental values taken from refs 6 (○, SMc, 500 K), 5 (▲, MauS, 600 K), and 8 (▼, S, 600 K).

Combining the two sets of experimental data gives an overall mean absolute deviation from theoretical results of 5.4 J mol^{-1} K^{-1} (28 comparisons).

Half-Reaction Entropies ($\Delta S_{1/2}$). Values for $\Delta S_{1/2}$, i.e., ΔS for the half-reactions A → AH$^+$, have been determined from the proton-transfer data by SMc[6] and by Sieck.[8] Our calculated values are compared with experimental values at 500 and 600 K in Table 4. The $\Delta S_{1/2}$ values all increase in going from 500 to 600 K, but within the narrow range of 0.7−2.6 J mol^{-1} K^{-1}. The small temperature dependence for proton-transfer reactions noted above is therefore not surprising. The mean and maximum absolute deviations between the SMc and theoretical $\Delta S_{1/2}$ values are 5.0 and 14.6 J mol^{-1} K^{-1}, respectively (18 comparisons). The Sieck results are in somewhat better

Table 4. Theoretical and Experimental Half-Reaction Entropies ($\Delta S_{1/2}$(A→AH$^+$), J mol^{-1} K^{-1})^a

A	$\Delta S_{1/2}^{500}$ theory	$\Delta S_{1/2}^{500}$ SMc^b	$\Delta S_{1/2}^{600}$ Sieck^c	$\Delta S_{1/2}^{600}$ theory
$(CH_3)_2NH$	−0.6	−6.3		0.5
CH_3NH_2	−4.7	−12.5		−3.5
pyrrole	10.4	4.2		11.6
NH_3	−6.0	−6.3		−5.3
$(CH_3)_2CO$	12.1	18.8	10.2	14.0
$(CH_3)_2CCH_2$	15.7	23.0	13.3	16.3
CH_3CH_2CN	11.5		12.1	14.0
$(CH_3)_2O$	20.8	18.8		22.7
CH_3OCHO	9.3	2.1	17.3	11.4
CH_3CN	10.0		12.7	12.6
CH_3CHO	5.7		15.3	7.8
CH_3OH	12.5	−2.1		14.8
CH_3CHCH_2	13.8	8.4		15.5
H_2S	5.6	6.3		7.1
H_2O	7.2	6.3		8.7
CS_2	35.7	46.0		37.6
C_2H_4	16.0	16.7		18.0
OCS	31.7	31.4		33.7
CO	7.5	12.6		9.5
CO_2	31.1	33.5		33.0
N_2	15.4	20.9		17.7

^{a} The entropy change for reaction 1 is given by $-\Delta S_{1/2} + S(H^+)$. Values of $S(H^+)$ are given in footnote a of Table 1. ^{b} From Szulejko and McMahon (ref 6); the reported values appear to be rounded to the nearest 0.5 cal mol^{-1} K^{-1} (2 J mol^{-1} K^{-1}). ^{c} From Sieck (ref 8).

Table 5. Comparison of Half-Reaction Entropies ($\Delta S_{1/2}^{600}$(A→AH$^+$), J mol^{-1} K^{-1}) Calculated by Using the E1, E2, and E3 Theoretical Models^a

	E3	E2	E1	E2 − E3	E1 − E3
CH_3NH_2	−3.5	−3.5	−3.1	b	0.4
CH_3CH_2CN	14.0	14.0	14.0	b	0.0
CH_3OCHO	11.4	11.4	11.0	b	−0.4
CH_3SH	10.1	10.1	9.3	b	−0.8
CH_3CHO	7.8	7.8	8.4	b	0.6
CH_3OH	14.8	14.8	14.9	b	0.1
CH_3CHCH_2	15.5	15.4	17.5	−0.1	2.0
$(CH_3)_2NH$	0.5	1.1	1.4	0.6	0.9
$CH_3CH_2NH_2$	−2.3	−2.0	−2.4	0.3	−0.1
$(CH_3)_2S$	15.2	15.6	16.2	0.4	1.0
$(CH_3)_2CO$	14.0	13.9	13.8	−0.1	−0.2
$(CH_3)_2CCH_2$	16.3	15.9	17.3	−0.4	1.0
$(CH_3)_2O$	22.7	23.2	26.1	0.5	3.4

^{a} The E1, E2, and E3 procedures are defined in the text. Note that for all the remaining systems in Table 7, E1, E2, and E3 are identical. ^{b} The E2 and E3 procedures are identical for single-rotor systems.

agreement with theory, with mean and maximum deviations of 3.6 and 7.5 J mol^{-1} K^{-1} (6 comparisons).

E1 and E2 Entropies. We have also computed $\Delta S_{1/2}$ values with the simpler E1 and E2 procedures[19] in all the cases where they differ from E3, i.e., for molecules containing torsional modes. The results are compared with E3 results in Table 5. In only two cases ($CH_3CH=CH_2$ and $(CH_3)_2O$) does the E1 procedure give protonation entropies that differ from the more accurate E3 values by more than 1 J mol^{-1} K^{-1}. The simplicity and reliability of E1 make it very suitable for general use. It should generally produce entropies with an accuracy (1−2 J mol^{-1} K^{-1}) significantly better than that accessible from van't Hoff plots for proton-transfer reactions (5−10 J mol^{-1} K^{-1}).

Absolute Enthalpies. We have used a combination of previously-published[10,12] and new G2 energies for 39 neutral molecules and their protonated forms to examine ΔG and ΔH values for protonation and proton-transfer reactions. The "absolute enthalpies" computed at the G2 level of theory for three temperatures (298, 500, and 600 K) are presented in Table S1 of the Supporting Information. Among the new G2 results

Table 6. Changes to Enthalpy Temperature Corrections Resulting from a Hindered Rotor Treatment for Internal Rotations Compared with Harmonic Oscillator Values (kJ mol^{-1})

A	H^{298} A	H^{298} AH$^+$	ΔH^{298} A $\rightarrow$ AH$^+$	ΔH^{600} A $\rightarrow$ AH$^+$
(CH$_3$)$_2$CCH$_2$	+0.4	−1.9	−2.3	−5.7
(CH$_3$)$_2$O	+0.3	+0.2	−0.1	−1.1
CH$_3$CHCH$_2$	+0.2	+0.1	−0.1	−0.9
CH$_3$OCHO	+0.2	−0.2	−0.4	−0.7
CH$_3$CHO	0.0	−0.2	−0.2	+0.2
(CH$_3$)$_2$CO	−0.7	−0.7	0.0	−0.1
CH$_3$OH	+0.2	+0.1	−0.1	−0.1

are those corresponding to the protonation of trimethylamine, pyridine, ethylamine, pyrrole, ethyl cyanide, and OCS. We examined two isomers of protonated OCS, denoted HSCO$^+$ and HOCS$^+$, at the G2 level, with the former lying 18.1 kJ mol^{-1} lower in energy at 0 K. Three isomers of protonated pyrrole (C$_4$H$_6$N$^+$) were investigated with G2(MP2) theory,[14] with the α carbons found to be the sites of highest proton affinity (contrary to what might be expected from a Mulliken population analysis on pyrrole). The α-carbon-protonated isomer lies 76.7 kJ mol^{-1} lower in energy than the N-protonated form and 19.1 kJ mol^{-1} lower in energy than the *β*-carbon-protonated form.

Enthalpy Temperature Corrections. Temperature corrections to the enthalpy are most often computed by using the harmonic oscillator approximation. The largest error from using this approximation should arise for nearly-free internal rotations. Seven half-reactions which seemed most likely to benefit from an improved treatment of torsional motion were examined, using the hindered rotor model and the Pitzer tables[20] in a manner entirely analogous to the way in which we computed the entropies. The corrections to the traditional all-HO results appear in Table 6. A significant correction for the half-reaction enthalpies is only found for the protonation of isobutene, in which nearly-free methyl rotations are produced. Use of the free rotor approximation for (CH$_3$)$_3$C$^+$, and the hindered rotor model and the Pitzer tables for isobutene, gives a G2 proton
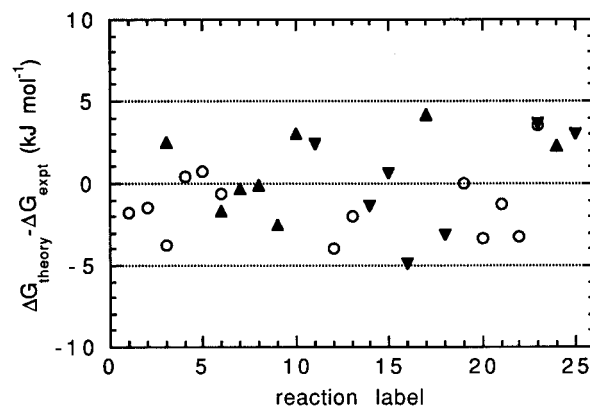
Figure 2. Differences between theoretical and experimental free energies at 600 K ($\Delta G_{theory} - \Delta G_{expt}$) for the 25 proton-transfer reactions of Table 7 and Figure 1. Experimental values from refs 6 (O, SMc), 5 (▲, MauS), and 8 (▼, S).

affinity at 298 K for isobutene of 804.4 kJ mol^{-1}, compared with 802.1 kJ mol^{-1} from strict use of the HO approximation.[9] At 600 K the improved G2 proton affinity value is 810.4 kJ mol^{-1}, compared with 804.7 kJ mol^{-1} with the HO approximation.

From the analysis in Table 6, it seems that reasonable results might generally be obtained by replacement of the HO enthalpy temperature corrections with free rotor contributions of $RT/2$ only for essentially-free internal rotations. In our set of systems, such a replacement would only be required for the three methyl rotations in (CH$_3$)$_3$C$^+$. The largest error for the proton affinity temperature correction for this set of proton affinities compared with values obtained by using a hindered rotor treatment throughout would then be just 0.4 kJ mol^{-1} at 298 K and 1.1 kJ mol^{-1} at 600 K.

Proton-Transfer Enthalpies and Free Energies. Calculated ΔH and ΔG values for the 25 proton-transfer reactions of Table 3 are compared with directly measured experimental values in Table 7. Deviations from experiment are plotted in Figures 2

Table 7. Theoretical and Experimental Free Energies and Enthalpies for Directly Measured Proton-Transfer Reactions (kJ mol^{-1})^{a,b}

	A	B	ΔG^{600} theory	ΔG^{600} SMc^c	ΔG^{600} MauS/S^d	ΔH^{600} theory	ΔH^{600} SMc^c	ΔH^{600} MauS/S^d
1	N$_2$	CO$_2$	−54.9	−53.1		−45.7	−44.8	
2	CO	OCS	−47.5	−46.0		−33.0	−33.9	
3	(CH$_3$)$_2$CCH$_2$	NH$_3$	−35.6	−31.9	−38.1	−48.5	−50.2	−53.6
4	CH$_3$NH$_2$	(CH$_3$)$_2$NH	−32.8	−33.2		−30.4	−29.7	
5	CH$_3$OCHO	(CH$_3$)$_2$CO	−31.8	−32.5		−30.2	−23.4	
6	NH$_3$	pyrrole	−30.2	−29.6	−28.5	−20.1	−23.8	−20.9
7	(CH$_3$)$_2$NH	(CH$_3$)$_3$N	−23.8		−23.5	−19.3		−20.5
8	(CH$_3$)$_2$CCH$_2$	(CH$_3$)$_2$S	−23.3		−23.2	−23.9		−28.5
9	pyridine	(CH$_3$)$_3$N	−22.4		−19.9	−21.6		−22.2
10	CH$_3$CH$_2$NH$_2$	pyridine	−20.7		−23.7	−15.3		−15.9
11	CH$_3$CH$_2$CN	(CH$_3$)$_2$CO	−19.7		−22.1	−19.7		−23.3
12	H$_2$O	H$_2$S	−18.5	−14.6		−19.4	−15.9	
13	pyrrole	CH$_3$NH$_2$	−18.1	−16.1		−27.1	−25.9	
14	CH$_3$CH$_2$CN	(CH$_3$)$_2$CCH$_2$	−15.7		−14.4	−14.4		−13.5
15	CH$_3$CN	CH$_3$CH$_2$CN	−13.4		−14.0	−12.6		−14.6
16	CH$_3$CHO	CH$_3$CN	−12.4		−7.5	−9.4		−9.3
17	(CH$_3$)$_2$S	NH$_3$	−12.3		−16.5	−24.6		−23.0
18	CH$_3$OCHO	CH$_3$CH$_2$CN	−12.1		−9.0	−10.5		−12.6
19	(CH$_3$)$_2$O	(CH$_3$)$_2$CCH$_2$	−11.8	−11.8		−15.7	−8.8	
20	CH$_3$CHCH$_2$	CH$_3$OH	−9.9	−6.6		−10.3	−14.2	
21	H$_2$O	CS$_2$	−9.9	−8.7		7.4	15.9	
22	CS$_2$	H$_2$S	−8.6	−5.4		−26.8	−31.0	
23	(CH$_3$)$_2$CCH$_2$	(CH$_3$)$_2$CO	−4.0	−7.5	−7.7	−5.3	−8.8	−9.6
24	(CH$_3$)$_2$NH	pyridine	−1.4		−3.7	2.3		0.8
25	CH$_3$CN	CH$_3$OCHO	−1.3	−4.3		−2.1		−1.8

^{a} Free energies and enthalpies of proton-transfer reactions AH$^+$ + B $\rightarrow$ A + BH$^+$. ^{b} Free energies calculated by using enthalpy values from Table S1 and entropies from Table 1. ^{c} From Szulejko and McMahon (ref 6). ^{d} From Mautner and Sieck (ref 5) and Sieck (ref 8).
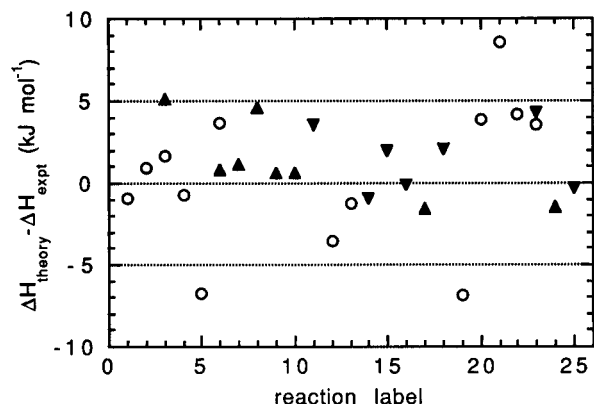
Figure 3. Differences between theoretical and experimental enthalpies at 600 K ($\Delta H_{theory} - \Delta H_{expt}$) for the 25 proton-transfer reactions of Table 7 and Figures 1 and 2. Experimental values from refs 6 ($\bigcirc$, SMc), 5 ($\blacktriangle$, MauS), and 8 ($\blacktriangledown$, S).

(ΔG) and 3 (ΔH). Figure 2 shows that theoretical and experimental ΔG values all agree to within 5 kJ mol^{-1}, reflecting the success of the G2 and E3 approaches. The agreement is still very good but is slightly worse for the enthalpy data in Figure 3. Note the possibility of very slight negative and positive biases in $\Delta G_{theory} - \Delta G_{SMc}$ (Figure 2) and $\Delta H_{theory} - \Delta H_{MauS/S}$ (Figure 3), respectively. The mean absolute deviations between the calculated ΔG^{600} values and the SMc (13 comparisons) and MauS/S (15 comparisons) values are just 2.0 and 2.4 kJ mol^{-1}, respectively, with maximum deviations of 3.9 and 4.9 kJ mol^{-1}. In the case of ΔH^{600}, the mean absolute deviations from the SMc and MauS/S results are 3.6 and 1.9 kJ mol^{-1}, respectively, with maximum deviations of 8.5 and 5.1 kJ mol^{-1}. If the theoretical results are compared with the combined set of experimental data, the overall mean absolute deviation for ΔG is 2.2 kJ mol^{-1} while that for ΔH is 2.7 kJ mol^{-1} (28 comparisons). Since the theoretical ΔH values are at least as accurate as the theoretical ΔG values (the latter being derived by using the calculated ΔH together with the calculated ΔS), the increased scatter in Figure 3 relative to Figure 2 is likely to be associated with uncertainties arising from the extraction of experimental ΔH values from van't Hoff plots.

Proton Affinities and Gas-Phase Basicities. Calculated proton affinities (PA), gas-phase basicities (ΔG), and half-reaction entropies ($\Delta S_{1/2}$) for 39 molecules at 298 and 600 K are presented in Table 8. The PA and ΔG values in Table 8 are the changes in enthalpy and free energy for the deprotonation reaction (eq 1), while the $\Delta S_{1/2}$ values refer to the half-reaction A $\rightarrow$ AH$^+$. Note that the proton affinity data reaffirm the observation[9] that PA^{600} − PA^{298} is consistently 2−5 kJ mol^{-1}, except for isobutene where the value is slightly higher at 6.3 kJ mol^{-1}. Not unexpectedly, the changes in gas-phase basicity are significantly greater, with $\Delta G^{600} - \Delta G^{298}$ varying between 24.9 and 37.6 kJ mol^{-1}. Finally, $\Delta S_{1/2}$ values also show a significant temperature variation, with $\Delta S_{1/2}^{600} - \Delta S_{1/2}^{298}$ varying between 2.8 and 8.4 J K^{-1} mol^{-1}, except for NH$_3$ (1.1 J K^{-1} mol^{-1}) and isobutene (0.1 J K^{-1} mol^{-1}).

The Szulejko−McMahon (SMc),[6] Mautner−Sieck (MauS),[5] and Sieck (S)[8] papers present relative proton affinity (ΔPA) and relative gas-phase basicity ($\Delta G°_{600}$) scales, with the selected reference compounds being carbon monoxide (SMc), isobutene (MauS), and acetonitrile (S), respectively. Although anchored absolute PA scales are also tabulated, we have chosen in the present study to compare *relative* theoretical and experimental values (ΔPA and ΔG, properly $\Delta\Delta G$) to avoid the introduction of anchoring errors. Thus, for the SMc data we compare

Table 8. Calculated Proton Affinities, Gas-Phase Basicities, and Half-Reaction Entropies[a,b]

	PA^{298}	PA^{600}	ΔG^{298}	ΔG^{600}	$\Delta S_{1/2}^{298}$	$\Delta S_{1/2}^{600}$
(CH$_3$)$_3$N	951.2	955.7	920.0	886.5	4.0	8.2
(CH$_3$)$_2$NH	931.7	936.4	898.6	862.7	−2.4	0.5
pyridine	929.8	934.1	898.1	864.1	2.2	6.7
CH$_3$CH$_2$NH$_2$	913.9	918.8	879.8	843.4	−5.4	−2.3
CH$_3$NH$_2$	901.0	906.0	866.6	829.9	−6.6	−3.5
pyrrole	874.0	878.9	844.1	811.8	8.8	11.6
NH$_3$	853.6	858.8	819.2	781.6	−6.4	−5.3
(CH$_3$)$_2$S	830.9	834.2	801.0	769.3	8.7	15.2
CH$_2$CO	825.0	829.8	793.2	759.0	2.4	5.4
(CH$_3$)$_2$CO	811.9	815.6	782.1	750.0	8.7	14.0
(CH$_3$)$_2$CCH$_2$	804.0	810.3	776.4	746.0	16.2	16.3
CS	795.6	799.1	764.2	730.8	3.3	9.5
CH$_3$CH$_2$CN	793.5	795.9	762.7	730.3	5.6	14.0
(CH$_3$)$_2$O	792.0	794.6	764.5	734.2	16.5	22.7
PH$_3$	784.8	788.9	750.4	713.8	−6.7	−1.7
C$_2$H$_3$CN	784.7	787.3	753.8	721.2	4.9	13.3
CH$_3$OCHO	782.2	785.4	751.3	718.2	5.1	11.4
CH$_3$CN	780.8	783.3	749.6	716.9	4.3	12.6
CH$_3$SH	776.4	780.1	745.0	712.2	3.6	10.1
HNC	772.6	777.1	740.2	705.4	0.1	4.0
CH$_3$CHO	770.2	773.9	738.1	704.5	1.3	7.8
CH$_2$S	768.7	772.2	739.4	708.3	10.8	16.9
CH$_3$OH	754.3	757.3	724.1	692.1	7.3	14.8
HCOOH	742.9	746.7	711.3	677.6	2.7	8.2
CH$_3$CHCH$_2$	744.3	747.0	714.9	682.2	10.2	15.5
HCN	712.0	715.2	680.7	647.6	4.0	10.6
CH$_2$O	711.8	715.9	682.2	650.5	9.5	14.3
H$_2$S	707.7	712.2	676.3	642.5	3.4	7.1
H$_2$O	688.4	692.8	657.3	624.0	4.8	8.7
CS$_2$	681.9	685.4	658.8	633.9	31.3	37.6
C$_2$H$_4$	681.9	685.6	653.1	622.4	12.2	18.0
OCS	626.4	629.6	601.9	575.8	26.6	33.7
CO	593.0	596.6	561.7	528.3	3.8	9.5
HBr	584.7	588.6	558.3	529.9	20.2	25.5
HCl	561.4	565.6	534.7	506.0	19.3	24.0
CO$_2$	539.3	542.7	514.7	488.5	26.4	33.0
N$_2$	493.9	497.0	464.6	433.6	10.5	17.7
HF	484.0	488.4	456.7	427.3	17.3	21.6
H$_2$	420.0	424.9	392.4	362.6	16.3	19.5

[a] Free energies calculated by using enthalpy values from Table S1 and entropies from Table 1. [b] PA and ΔG in kJ mol^{-1}; $\Delta S_{1/2}$ in J mol^{-1} K^{-1}.

theoretical and experimental values relative to those for CO while for the MauS and S data we compare theoretical and experimental values relative to those for isobutene and CH$_3$-CN, respectively. Deviations between theory and experiment in the resultant ΔG^{600} and ΔPA^{600} values are displayed in Figures 4 and 5, respectively.

Examination of Figure 4 shows good general agreement between theoretical and experimental ΔG values, the differences exceeding 5 kJ mol^{-1} in only a small number of cases. An intriguing observation, however, is that the deviations between the theoretical ΔG values and the SMc set of experimental ΔG values appear to be correlated with the magnitude of the ΔG, i.e. with where the molecule is located on the gas-phase basicity ladder. We noted above the possibility of a slight bias in ΔG values for proton-transfer reactions (Figure 2, Table 7), and indeed a closer examination of the data in Figure 2 reveals that the SMc values are on average 1.3 kJ mol^{-1} less negative than the theoretical values (while the MauS/S values are on average 0.5 kJ mol^{-1} more negative than the theoretical values). It appears that these very small average differences in the proton-transfer ΔG values lead to a relative contraction of the SMc ΔG scale and a possible expansion of the 1991 MauS ΔG scale. It is unlikely that errors in theoretical gas-phase basicities should be dependent on the magnitude of ΔG, and we therefore feel that any slopes in Figure 4 are more likely to be attributable to the experimental scales. They may partly reflect a cumulative
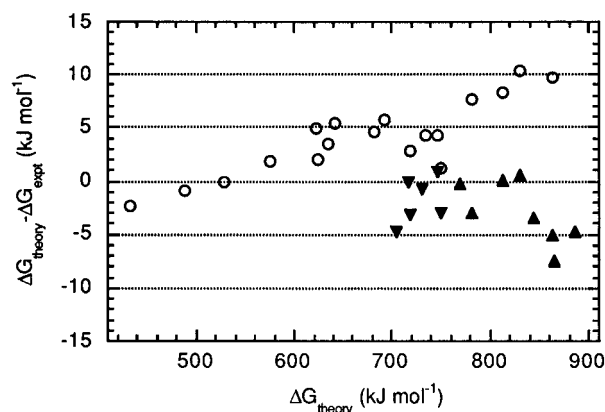
Figure 4. Differences between theoretical and experimental relative gas-phase basicities at 600 K ($\Delta G_{theory} - \Delta G_{expt}$), plotted against the theoretical magnitude of the gas-phase basicity. Experimental values from refs 6 (○, SMc), 5 (▲, MauS), and 8 (▼, S). See text for the choice of reference values.
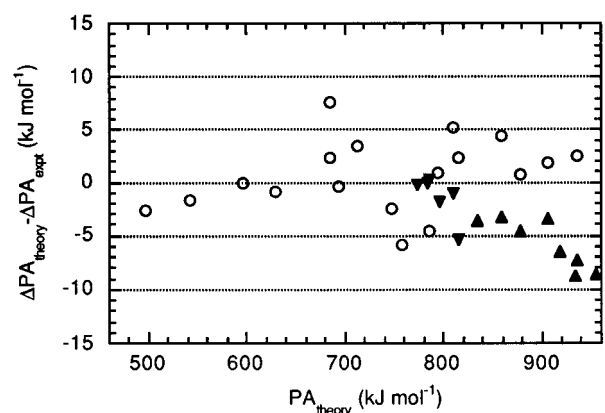

Figure 5. Differences between theoretical and experimental relative proton affinities at 600 K ($\Delta PA_{theory} - \Delta PA_{expt}$), plotted against the theoretical magnitude of the proton affinity. Experimental values from refs 6 (○, SMc), 5 (▲, MauS), and 8 (▼, S). See text for the choice of reference values.

effect inherent in a ladder-building procedure, although this is probably reduced through overdetermination.

The equivalent plot for proton affinities (enthalpies) appears as Figure 5. Again there is good general agreement between theory and experiment, the majority of the ΔPA values agreeing to within 5 kJ mol^{-1}. The MauS/S PA data appear correlated

with the magnitude of the proton affinity, which is consistent with the possible slight bias noted for proton-transfer reactions (Figure 3, Table 7), but there is no clear trend of this type for the SMc data.

Global expansions or contractions of ΔG and PA scales derived from single-temperature proton-transfer equilibrium experiments have been observed previously, and adjustments of up to 11% in temperature assignment have been proposed for these cases. In the present situation, small global corrections of 3−4% to the SMc ΔG ladder and the MauS/S PA ladder would bring both into ~5 kJ mol^{-1} agreement with theory and with one another, a level of agreement already noted for proton-transfer free energies and enthalpies.

Concluding Remarks

Statistical gas-phase entropies have been computed for 25 proton-transfer reactions, and the results combined with G2 enthalpies for comparison with results determined from variable-temperature equilibrium measurements. Agreement with experimental thermodynamic data for ΔG and ΔH for proton-transfer reactions is excellent, with mean absolute deviations of 2.2 kJ mol^{-1} for ΔG and 2.7 kJ mol^{-1} for ΔH. For ΔS, the mean absolute deviation is 5.4 J mol^{-1} K^{-1}, which largely reflects experimental uncertainty since the theoretical results are believed to be accurate to about 1 J mol^{-1} K^{-1}. Theoretical proton affinity (ΔH) and gas-phase basicity (ΔG) scales including 39 molecules have been assembled and are in very good agreement with experimental scales. The small deviations that do exist between theoretical and experimental gas-phase basicities and proton affinities show some systematic dependences on proton affinity magnitude, which suggests that there may be small relative expansions or contractions of the experimental scales in the affected cases.

Supporting Information Available: Calculated G2 enthalpies at 0, 298, and 600 K for 39 molecules (Table S1) (1 page). See any current masthead page for ordering and Internet access instructions.

JA970891J