ELSEVIER

International Journal of Mass Spectrometry 195/196 (2000) 215–223

International Journal of Mass Spectrometry

The temperature dependence of absolute gas phase acidities

John E. Bartmess[a,]*, Jason L. Pittman[a], Jeremiah A. Aeschleman[b],
Carol A. Deakyne[b]

[a]*Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600, USA*
[b]*Department of Chemistry, Eastern Illinois University, Charleston, IL 61920-3099, USA*

Received 3 June 1999; accepted 10 September 1999

Abstract

Using both ab initio and semiempirical calculations, the temperature dependence of the thermochemical cycle relating gas phase enthalpies of acidity to electron affinities and bond dissociation energies is examined. In almost all cases, the effect of temperature is less than the uncertainties in the thermochemical quantities themselves. (Int J Mass Spectrom 195/196 (2000) 215–223) © 2000 Elsevier Science B.V.

Keywords: Thermochemical; Gas phase anthalpy; Acidity; Electron affinity; Bond dissociation energy

---

1. Introduction

The majority of the techniques [1] that are used to determine numeric values for gas phase acidities [2] yield relative acidity values [3]. To assign absolute values to these scales of relative acidities, a thermochemical cycle has most commonly been used. This cycle relates the enthalpy of acidity $\Delta H_{acid}(AH)$ to (1) the homolytic bond dissociation energy of the acid AH, BDE(A − H), (2) the ionization energy of the hydrogen atom, IE(H·), and (3) the electron affinity of the A· radical, EA(A·), as shown in Scheme 1.

$$\begin{tikzcd}
AH \arrow[r, "\Delta H_{acid}(AH)"] \arrow[d, "BDE(A-H)"'] & A^- + H^+ \\
A\cdot + H\cdot \arrow[r, "IE(H^\cdot)"] & A\cdot + H^+ + e^- \arrow[u, "-EA(A\cdot)"']
\end{tikzcd}$$

$$\Delta H_{acid}(AH) = BDE(A-H) + IE(H\cdot) - EA(A\cdot) \tag{1}$$

There is an assumption built into this thermochemical cycle, however, that has not been experimentally tested. The enthalpy of acidity and the bond dissociation energy are quantities commonly available at 298 K. Ionization energies and electron affinities [4,5] are usually reported as 0 K threshold values, because the 0–0 transition is relatively easy to assign in the experiments measuring these values. Obtaining a 298 K value for these quantities, from an analysis of higher energy transitions, is more difficult. Values of the EA and IE at 298 K are technically needed for Scheme 1, because most of the available experimental gas phase acidities were either measured near that temperature, or at higher temperatures (500–600 K) [6] and then related to 298 K. In order to justify the use of 0 K data in a thermochemical cycle set at 298

---

* Corresponding author.

Dedicated to Bob Squires for his many seminal contributions to mass spectrometry and ion chemistry.

1387-3806/00/$20.00 © 2000 Elsevier Science B.V. All rights reserved
PII S1387-3806(99)00219-5

Table 1
Ab initio results, analyzed with unscaled vibrational frequencies

System[a]	Level[b]	ΔIHC_{298}[d]	EA_0[e]	EA_{298}[f]	$IHC(X\cdot)$[g]	$IHC(X^-)$[h]
HO^-	HF	0.00	−34.57	−34.57	2.074	2.074
HO^-	MP2	0.00	38.30	38.30	2.074	2.074
MeO^-	HF	0.05	−21.56	−21.52	2.447	2.395
MeO^-	MP2	0.05	33.37	33.41	2.463	2.414
EtO^-	HF	0.34	−19.30	−18.96	3.245	2.901
EtO^-	MP2	0.15	37.24	37.40	3.114	2.961
$MeCO_2^-$	HF	0.04	28.41	28.46	3.331	3.296
$MeCO_2^-$	MP2	0.09	79.79	79.88	3.449	3.357
PhO^-	HF	0.14	−4.77	−4.61	3.780	3.636
NH_2^-	HF	0.00	−50.30	−50.30	2.371	2.371
NH_2^-	MP2	0.00	9.96	9.96	2.373	2.373
Me_2N^-	HF	0.38	−40.06	−39.66	3.480	3.104
Me_2N^-	MP2	0.42	7.03	7.45	3.566	3.146
H_2NNH^-	HF	−0.12	−57.10	−57.21	2.509	2.629
H_2NNH^-	MP2	−0.06	−9.09	−9.16	2.565	2.626
$MeNHNMe^-$	HF	0.09	−49.42	−49.33	3.997	3.906
$MeNHNMe^-$	MP2	0.10	−6.04	−5.95	4.096	4.000
CH_3^-	HF	0.25	−57.03	−56.78	2.633	2.383
CH_3^-	MP2	0.11	−8.74	−8.62	2.531	2.424
$MeCH_2^-$	HF	0.31	−58.11	−57.81	3.001	2.696
$MeCH_2^-$	MP2	0.23	−14.11	−13.88	3.018	2.784
Me_3C^-	HF	0.50	−54.45	−53.94	4.418	3.916
Me_3C^-	MP2	0.46	−7.93	−7.47	4.432	3.973
$PhCH_2^-$	HF	0.01	−38.76	−38.76	4.050	4.037
$MeCC^-$	HF	0.06	12.68	12.73	2.947	2.888
$MeCC^-$	MP2	−0.30	69.11	68.81	2.848	3.148
MeS^-	HF	0.07	8.21	8.28	2.546	2.475
MeS^-	MP2	0.07	32.56	32.63	2.563	2.497

[a] Anion of the anion/radical pair.
[b] HF: HF/6-31G(*d*)//HF/6-31G(*d*); MP2: MP2/6-31+G(*d*, *p*)//MP2/6-31+G(*d*, *p*).
[c] In Hartrees.
[d] Discrepancy of Eqs. (8) and (9), kcal mol^{-1}.
[e] $\Delta H_0(X\cdot) - \Delta H_0(X^-)$, eV.
[f] $\Delta H_{298}(X\cdot) - \Delta H_{298}(X^-)$, eV.
[g] $\Delta H_{298}(X\cdot) - \Delta H_0(X\cdot)$, kcal mol^{-1}.
[h] $\Delta H_{298}(X^-) - \Delta H_0(X^-)$, kcal mol^{-1}.

K, it has been assumed [7] that there is negligible temperature dependence of the enthalpy of electron transfer reaction (2)

$$A\cdot + H\cdot \rightarrow A^- + H^+ \tag{2}$$

This is equivalent to

$$IE_{298K}(H\cdot) - EA_{298K}(A\cdot) = IE_{0K}(H\cdot) - EA_{0K}(A\cdot) \tag{3}$$

Now, because

$$IE(H\cdot) = \Delta_f H(H^+) + \Delta_f H(e^-) - \Delta_f H(H\cdot) \tag{4}$$

$$EA(A\cdot) = \Delta_f H(A\cdot) + \Delta_f H(e^-) - \Delta_f H(A^-) \tag{5}$$

and because the integrated heat capacity IHC(X) is defined as

$$IHC_T(X) = \Delta_f H_T(X) - \Delta_f H_{0K}(X) \tag{6}$$

then for (2) to be temperature independent, Eq. (7) must hold

$$IHC_T(H\cdot) - IHC_T(H^+) = IHC_T(A^-) - IHC_T(A\cdot) \tag{7}$$

The evaluation of $\mathrm{IHC}_T(\mathrm{H}^+)$ and $\mathrm{IHC}_T(\mathrm{H}\cdot)$ is straightforward, based on a statistical mechanics evaluation. The exact numeric value for the proton depends slightly on the convention used for ion thermochemistry [8], but in either convention, both integrated heat capacities are about 1.481 kcal mol^{-1} [9], and cancel within a few cal mol^{-1}. Thus, to verify assumption (3), it is sufficient to show that

$$\mathrm{IHC}_T(\mathrm{A}^-) = \mathrm{IHC}_T(\mathrm{A}\cdot) \tag{8}$$

to within some desired accuracy, on the order of the uncertainty for the whole cycle in Scheme (1). Using a temperature-dependent version of Eq. (5), it can be shown that this is equivalent to

$$\mathrm{EA}_{298\mathrm{K}}(\mathrm{A}\cdot) = \mathrm{EA}_{0\mathrm{K}}(\mathrm{A}\cdot) \tag{9}$$

Any deviation from this condition will be referred to as a "discrepancy."

Lias and Ausloos [10] presented an argument based on statistical mechanics [11] that rationalized the near equivalence of the integrated heat capacity of a species M and its radical ion $\mathrm{M}^{+\cdot}$. The translational and rotational integrated heat capacities cancel for the ion and neutral, because of the essentially identical masses and near-equivalent gross structures. The vibrational integrated heat capacity will depend somewhat on the changes in bonding associated with the removal of the electron, and whether it is from a bonding or nonbonding orbital, but the majority of vibrations will cancel reasonably well. The electronic term may be appreciable, because of the possibility of low-lying electronic states in M and $\mathrm{M}^{+\cdot}$. However, Lias and Ausloos concluded that below 400 K, only splittings of the energies of degenerate states on the order of 0.05–3.0 kcal mol^{-1} can contribute significantly to the heat capacity and heat of formation of a species. The maximum change in the heat of formation, with a splitting of ~1.0 kcal mol^{-1}, is only 0.2 kcal mol^{-1}. Thus the electronic term is probably negligible. It was thus expected that for M and $\mathrm{M}^{+\cdot}$, the difference in integrated heat capacity would be small. For A^- and A· in the present work, a similar set of arguments should hold. Although such anions may have bound excited states, these are usually 15 kcal mol^{-1} or more above the ground state, where they would have negligible effect.

Experimental evaluation of integrated heat capacities is difficult for reactive species such as single ions and radicals. We have therefore utilized molecular orbital calculations as an approach to determining how effective the cancellation of vibrational and rotational effects might be.

2. Calculations

The ab initio calculations were carried out with use of the GAUSSIAN 94 series of programs [12] on a Convex 3820 and Cray C90 computer. Each species was fully optimized at both the HF/6-31G(*d*) and MP2/6-31+G(*d*, *p*) levels of theory in order to assess the effects of basis set size and electron correlation on the results. The cores of the heavy atoms were kept frozen for the MP2 calculations [13]. Normal-mode vibrational frequencies were obtained at both levels of theory in order to confirm that the optimized structures are equilibrium structures and to determine zero-point energies (ZPEs) and heat capacity corrections [14]. The enthalpy of each neutral molecule and negative ion was determined using both scaled and unscaled frequencies. The HF/6-31G(*d*) and MP2/6-31+G(*d*, *p*) vibrational frequencies were scaled by the usual factors of 0.8929 and 0.9427, respectively [15].

The semiempirical calculations were carried out using the MOPAC 6 package [16] at the AM1 level [17]. These included calculations on the acid forms, to calculate the various thermochemical parameters for a series of anions and the corresponding radicals and conjugate acids, many of which were too large to handle at the ab initio level. All geometries were fully optimized at the "precise" level. Certain radicals, notably isopropoxy, proved incapable of convergence under any conditions in the force calculations.

Although it is well established that AM1 does not yield accurate absolute gas phase acidities, especially in the cases of acids with localized anions and small (di- or tri-atomic) species [18], it still provides rea-

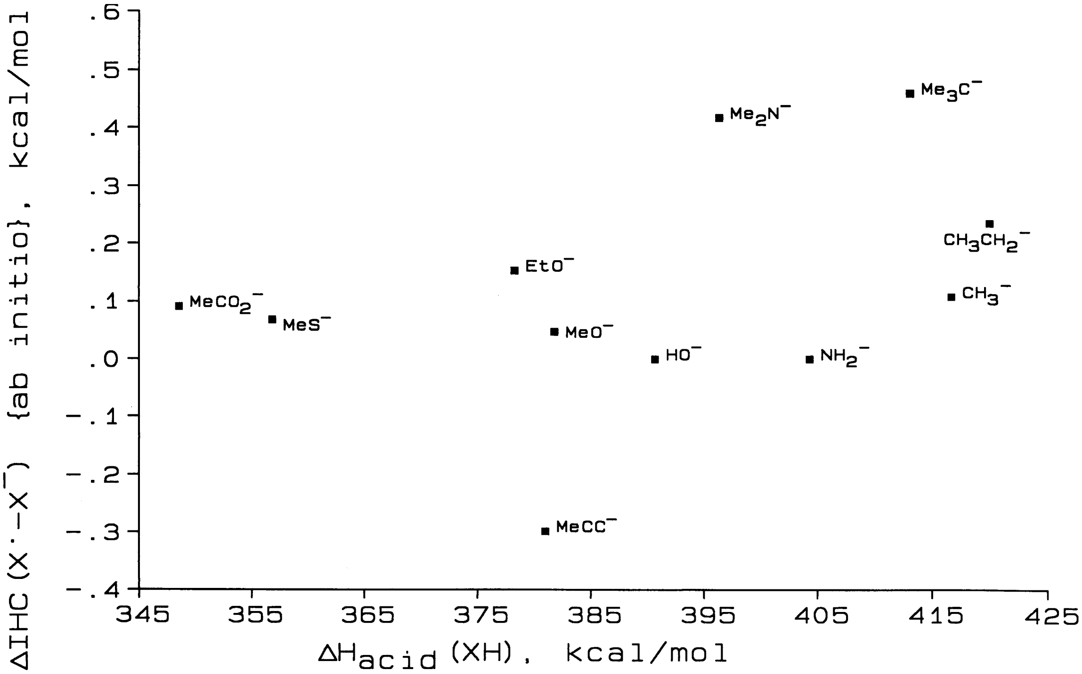

Fig. 1. Temperature dependence of the integrated heat capacity from MP2 ab initio calculations vs. experimental gas phase anion proton affinity.

sonable acidity values for many functional groups. It is also amenable to calculating the large structures examined here as possible cases where Eq. (8) might not hold.

The results of the ab initio calculations are given in Table 1 and Fig. 1, and the semiempirical ones in Table 2 and Fig. 2. For the ab initio calculations, scaling the frequencies by the usual factors made a worst-case change in the ΔIHCs of 0.029 kcal mol^{-1} [for Me_3C^- at the HF/6-31G(*d*) level] from the unscaled integrated heat capacities, and a root mean square (rms) change of 0.011 kcal mol^{-1} (combining the data from both levels). We thus use the unscaled values alone.

3. Discussion

The molecules chosen for inclusion in this study range over a variety of structural types, in order to examine whether the possible cancellation of temperature effects in Scheme 1 is limited to a few structures, or is more general. Small localized species (CH_3^-, NH_2^-, HO^-, HS^-) were included, plus alkylated and substituted derivatives [MeO^-, EtO^-, $tBuO^-$, $CF_3CH_2O^-$, $(CF_3)_3CO^-$, PhO^-, Me_2N^-, MeS^-), carbanions ($MeCH_2^-$, Me_3C^-, cyclopentadienide$^-$, $PhCH_2^-$, $MeC{\equiv}C^-$), carboxylates ($MeCO_2^-$, $CF_3CO_2)^-$, and enolate-type species ($CH_2{=}C(CH_3)O^-$, $CH_2{=}C(CF_3)O^-$, $PhN{=}C(Me)O^-$].

Certain species were included because it was thought that there might be an appreciable difference in internal rotation between the radical and anion. Such cases would be likely candidates for the failure of Eqs. (8) or (9). $MeNHNMe^-$ and H_2NNH^- are two such structures: there should be a considerable barrier to rotation in the radical, due to delocalization of the radical site to the adjacent equivalent two-electron lone pair, that is not possible in the closed-shell anion. Other species that had major torsional effects due to large rotors were paired with rigid equivalents, such as Ph_2CH^- versus fluorenide. Deprotonated acetani-

Table 2
AM1 results

						ΔH_{acid}[g]	
System[a]	ΔIHC[b]	$\delta\Delta H_f$[c]	EA[d]	ΔC_p[e]	ΔS[f]	expt	AM1
HO^-	0.000	15.055	42.147[h]	0.000	0.047	390.7	410.8
MeO^-	0.030	34.804	36.205[h]	0.405	0.184	381.8	384.2
EtO^-	0.133	35.808	39.549[h]	0.961	0.768	378.3	383.1
$tBuO^-$	0.177	41.574	44.092[h]	0.209	1.815	374.6	383.1
$CF_3CH_2O^-$	0.085	60.419	58.900[h]	0.324	1.607	361.7	355.2
$(CF_3)_3CO^-$	0.582	99.487	87.000[i]	1.960	6.235	331.6	332.3
$MeCO_2^-$	0.081	71.340	70.800[i]	0.375	0.603	348.6	353.3
PhO^-	0.167	45.674	51.955[h]	0.790	1.159	349.2	346.7
$CF_3CO_2^-$	0.007	103.942	95.800[i]	0.028	−0.074	323.8	321.1
NH_2^-	0.000	−14.739	17.896[h]	0.017	−0.094	403.6	425.5
Me_2N^-	0.207	3.629	8.700[i]	0.464	2.604	396.4	393.7
$MeNHNMe^-$	0.297	−4.273	—	0.802	5.138	—	382.5
CH_3^-	−0.179	−27.768	1.845[h]	−0.885	−0.942	416.7	432.2
$MeCH_2^-$	0.049	−16.360	−6.000[i]	−0.171	4.797	420.1	417.6
Me_3C^-	0.055	−5.697	−3.600[i]	0.384	1.520	413.1	398.0
$PhCH_2^-$	0.121	17.782	21.031[h]	0.616	0.673	380.6	372.0
Ph_2CH^-	0.203	28.924	31.400[i]	0.937	1.782	363.6	352.8
$C_5H_5^-$	0.167	36.741	41.186[h]	1.164	0.907	353.9	353.8
Fluorenide$^-$	0.156	40.015	43.100[h]	0.794	1.085	351.7	347.5
$CH_2{=}C(Me)O^-$	0.184	28.837	40.518[h]	0.860	−0.598	369.1	370.6
$PhN{=}C(Me)O^-$	0.193	52.104	65.100[i]	0.940	1.274	347.5	346.2
$CH_2{=}C(CF_3)O^-$	0.198	54.434	59.500[h]	0.600	1.812	349.2	345.0
$MeCC^-$	0.193	56.770	62.678[h]	0.641	1.269	381.0	397.2
HS^-	0.110	55.990	53.431[h]	0.003	0.015	351.2	352.6
MeS^-	0.059	46.252	43.146[h]	0.561	0.215	356.9	353.1

[a] Anion of the anion/radical pair.
[b] Discrepancy of Eqs. (8) and (9), kcal mol^{-1}.
[c] $\Delta_f H_0(X\cdot) - \Delta_f H_0(X^-)$, kcal mol^{-1}, AM1, corresponding to the electron affinity.
[d] Experimental electron affinity, kcal mol^{-1} [3].
[e] $C_p(X\cdot) - C_p(X^-)$ at 298 K, cal mol^{-1} K^{-1}, AM1.
[f] $S(X\cdot) - S(X^-)$ at 298 K, cal mol^{-1} K^{-1}, AM1.
[g] Gas phase acidity, 298 K, kcal mol^{-1}. Experimental from [3].
[h] Experimentally determined, [3].
[i] From an inversion of Scheme 1.

lide, $PhN{=}C(CH_3)O^-$, was included, because it appears from the temperature dependence of experimental gas phase acidities [19] that there may be an appreciable heat capacity effect on this acidity: unlike most other gas phase acids, its acidity changes appreciably between 300 K and 600 K.

For the ab initio quantities, the discrepancy in Eqs. (8) or (9) ranges from -0.3 kcal mol^{-1} ($MeC{\equiv}C^-$) to 0.5 kcal mol^{-1} (Me_3C^-) at the MP2 level. Although the ΔIHC values are not identical for the HF and MP2 calculations, the overall trends and conclusions are the same for both sets of data. The expected "worst-case" IHC for 1,2-dimethylhydrazide is only 0.10 kcal mol^{-1}. The value for HO^- agrees with that in the standard thermochemical references [9,20] to within 50 cal mol^{-1}, when corrected to the same standard state [8]. From Fig. 1 it is evident that the propynide is an outlier relative to the other points, but the anion and radical are also of a unique type compared to the others. Similarly, at the AM1 level, the discrepancy ranges from 0–0.30 kcal mol^{-1}, with outliers of CH_3^- at -0.18 and $(CF_3)_3CO^-$ at $+0.58$ kcal mol^{-1}. The latter is probably due to a flaw in the semiempirical method; for $(CF_3)_3CO^-$ the C–C and C–O bond

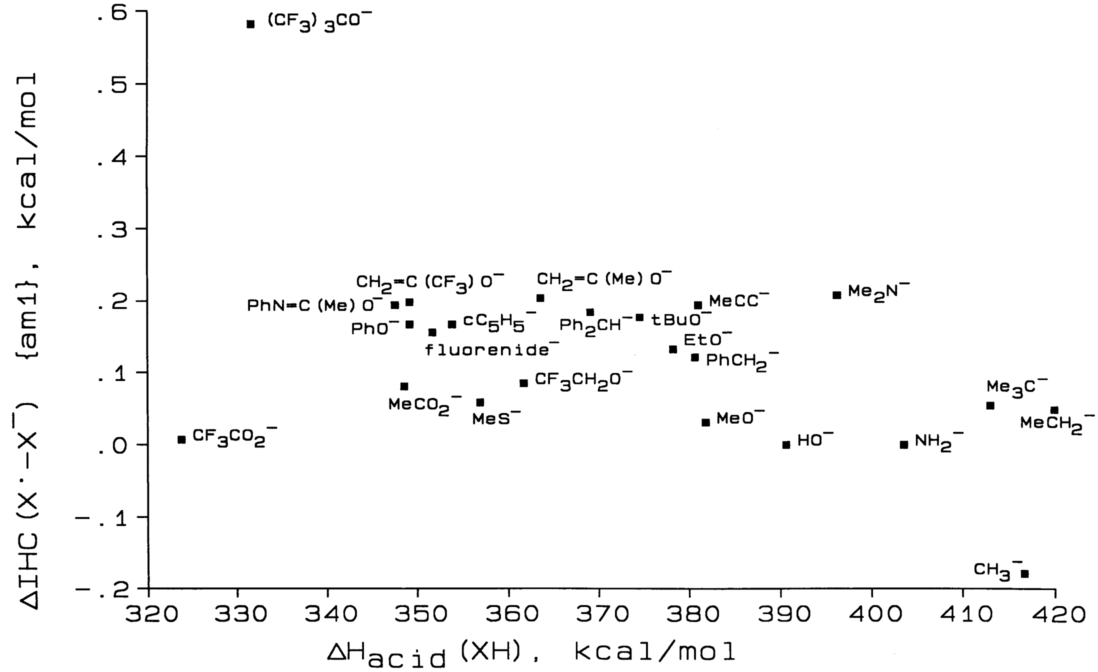

Fig. 2. Temperature dependence of the integrated heat capacity from AM1 calculations vs. experimental gas phase anion proton affinity.

lengths are calculated at the AM1 level to be 1.62 Å and 1.27 Å, respectively, compared to the more reasonable values of 1.55 Å and 1.32 Å, respectively, in $(CH_3)_3CO^-$.

There is a slight trend in the ab initio values of larger molecules within a class having larger discrepancies: $NH_2NH^- < MeNHNMe^-$, $HO^- < MeO^- < EtO^-$, $NH_2^- < Me_2N^-$, and $CH_3^- < MeCH_2^- < Me_3C^-$. The total range here, however, is only at most 0.40 kcal mol^{-1}. Similar tendencies are observed in the AM1 results.

As a check on the reliability of the calculations, it is noted that the ab initio values at the MP2 level reproduce the experimental 0 K electron affinities with a standard deviation of 0.30 eV (0.28 eV if the third-row anion MeS^- is omitted). If the small anions HO^-, NH_2^-, and CH_3^- are omitted [18], the AM1 method yields electron affinities with a standard deviation of 0.23 eV from the experimental values. A reasonable correlation ($r = 0.984$) between the calculated AM1 and experimental values is found. The slope of the line is 1.11, and the largest deviations, for PhNCOMe and $(CF_3)_3CO$, are for points where the experimental electron affinity was not directly measured, but rather estimated from the gas phase acidity and bond strengths of questionable accuracy, using an inversion of Scheme 1. If those radicals with EAs derived from Scheme 1 are excluded, the remaining 12 points have a slope of 0.99 ± 0.10, an intercept within a standard deviation of zero, and $r = 0.950$. It thus appears that both ab initio and semiempirical calculations yield reasonable enthalpy values.

Are the temperature effects found here small enough to be negligible with respect to the other uncertainties in the values obtained from Scheme 1? The available data are presented in Table 3. It is clear that in most cases it is the uncertainty in the BDE that is the largest factor in the uncertainty of the absolute acidity [21]. The discrepancies calculated here are smaller than the uncertainties for all the acids except H_2/D_2, water, and the hydrogen halides, plus a few

Table 3
Enthalpies of acidity from Scheme 1

Acid	ΔH_{acid}[a]	EA(A·)[b]	Ref.	BDE(A−H)[c]	Ref.
D2	402.3 ± 0.0	17.4 ± 0.0	22	105.0 ± 0.0	20
H2	400.4 ± 0.0	17.4 ± 0.0	22	104.2 ± 0.0	20
HI	314.3 ± 0.0	70.5 ± 0.0	23	71.3 ± 0.0	20
D_2O	391.2 ± 0.1	42.1 ± 0.0	24	119.7 ± 0.1	20
H_2O	390.7 ± 0.1	42.1 ± 0.0	24	119.3 ± 0.1	20
HBr	323.5 ± 0.1	77.6 ± 0.0	25	87.5 ± 0.1	20
HCl	333.4 ± 0.1	83.3 ± 0.0	26	103.2 ± 0.1	20
H_2Se	342.6 ± 0.2	51.0 ± 0.0	27	80.1 ± 0.2	28
HONO	340.2 ± 0.2	52.4 ± 0.1	29	79.1 ± 0.2	20
HF	371.6 ± 0.2	78.4 ± 0.0	25	136.4 ± 0.2	20
$H_2C{=}O$	393.5 ± 0.7	7.2 ± 0.1	30	87.1 ± 0.7	31
CH_4	416.7 ± 0.8	1.8 ± 0.7	32	104.9 ± 0.3	33
SiH_4	372.8 ± 0.8	32.4 ± 0.3	34	91.6 ± 0.8	35
$CH_3CH{=}O$[d]	389.8 ± 0.9	9.8 ± 0.9	36	85.9 ± 0.4	37
H_2S	350.7 ± 0.9	53.4 ± 0.0	38	90.6 ± 0.9	20
NH_3	404.2 ± 0.9	17.9 ± 0.9	39	108.5 ± 0.3	20
EtOH	378.3 ± 1.0	39.5 ± 0.2	40	104.2 ± 1.0	37
Toluene	380.6 ± 1.0	21.0 ± 0.1	41	88.0 ± 1.0	37
HSCN	325.3 ± 1.1	81.6 ± 0.1	42	93.3 ± 1.1	43
MeOH	381.8 ± 1.1	36.2 ± 0.5	44	104.4 ± 1.0	37
$(CH_2{=}CH)_2CH_2$	369.2 ± 1.2	21.0 ± 0.7	45	76.6 ± 1.0	46
*i*PrOH	375.9 ± 1.2	42.4 ± 0.7	47	104.7 ± 1.0	37
Cyclopentadiene	353.6 ± 1.3	41.2 ± 0.5	48	81.2 ± 1.2	49
*n*PrOH	375.7 ± 1.3	41.3 ± 0.8	47	103.4 ± 1.0	37
$CH_2{=}CHCH_3$	389.1 ± 1.5	11.1 ± 0.2	50	86.6 ± 1.5	51
Me_2S	390.2 ± 1.5	20.0 ± 1.2	52	96.6 ± 1.0	53
PH_3	363.7 ± 1.6	29.3 ± 0.2	54	79.4 ± 1.6	20
*t*BuOH	374.6 ± 1.6	44.1 ± 1.2	47	105.1 ± 1.0	37
Thiophenol	335.6 ± 1.7	57.0 ± 1.4	55	79.0 ± 1.0	56
*t*BuCH$_2$OH	371.4 ± 1.9	44.5 ± 1.2	57	102.3 ± 1.5	37
HOOH	375.6 ± 2.1	25.1 ± 0.1	58	86.9 ± 0.7	20
CH2=C(Me)CH3	387.0 ± 2.0	11.6 ± 0.1	50	85.0 ± 2.0	59
CH2=C=CH2	380.0 ± 2.0	21.2 ± 0.2	60	87.6 ± 2.0	37
HCN	348.3 ± 2.0	89.1 ± 0.1	42	123.8 ± 2.0	37
MeSH	357.6 ± 2.0	43.1 ± 0.3	52	87.1 ± 2.0	61
Phenol	348.1 ± 2.0	52.0 ± 0.1	41	86.5 ± 2.0	62
$SiMe_4$	390.9 ± 2.0	21.9 ± 0.3	63	99.2 ± 2.0	64
$PhCOCH_3$	359.0 ± 2.1	47.6 ± 1.8	65	93.0 ± 1.0	66
HN_3	343.9 ± 2.2	63.7 ± 1.0	67	94.0 ± 2.0	66
$EtCOCH_2Me$	362.8 ± 2.3	38.8 ± 1.2	65	88.0 ± 2.0	68
*i*PrCOCHMe$_2$	364.8 ± 2.3	33.8 ± 1.2	65	85.0 ± 2.0	68
CH_3CO_2Me	364.7 ± 2.4	41.5 ± 1.4	65	92.6 ± 2.0	69
$HSiF_3$	345.7 ± 2.5	68.0 ± 2.3	70	100.1 ± 1.0	64
Me_3GeH	363.4 ± 2.5	31.9 ± 0.7	71	81.7 ± 2.4	72
*t*BuCOCH$_3$	365.1 ± 2.5	42.5 ± 1.5	65	94.0 ± 2.0	68
GeH_4	356.0 ± 2.7	40.1 ± 1.0	73	82.5 ± 2.5	74
Heptatriene	364.8 ± 3.1	29.3 ± 0.7	45	80.5 ± 3.0	75
HNCO	340.9 ± 3.8	83.2 ± 0.1	42	110.5 ± 3.8	76
Phenalene	350.9 ± 3.8	24.7 ± 2.3	77	62.0 ± 3.0	78
TeH_2	332.0 ± 4.6	48.5 ± 0.3	79	66.9 ± 4.6	80

[a] Enthalpy of acidity from Scheme 1, kcal mol^{-1}.

[b] Electron affinity, kcal mol^{-1}, from listed reference.

[c] Bond dissociation energy, kcal mol^{-1}, from listed reference.

[d] Aldehydic hydrogen is the acidic one.

others. The net effect is that the acidities from Scheme 1 appear to be slightly too weak.

3. Conclusions

The basic thesis that Scheme 1 contains a self-canceling effect to make it temperature independent, is supported by both ab initio and semiempirical calculations. For most of the species examined, the temperature effect found is less than the known uncertainties for the individual steps in Scheme 1.

Acknowledgement

We thank Dr. S.G. Lias for helpful discussions.

References

[1] Techniques for the Study of Ion-Molecule Reactions, J.M. Farrar, W.H. Saunders Jr. (Eds.), Techniques of Chemistry, Vol. 20, Wiley, New York, 1988.

[2] The term “gas phase acidity” strictly refers to free energy, whereas the enthalpic term is “anion proton affinity.” Because of the accuracy of statistical mechanics by which the entropy of acidity can be calculated for many such acids, and the small range of such entropic effects, they are often used interchangeably in a loose sense.

[3] J.E. Bartmess, Negative Ion Energetics Data, in W.G. Mallard, P.J. Linstrom (Eds.), The NIST Chemistry WebBook, NIST Standard Reference Database Number 69, March 1998, National Institute of Standards and Technology, Gaithersburg, MD, 20899 (http://webbook.nist.gov).

[4] S.G. Lias, Ionization Energy Evaluation, in [3].

[5] D.M. Wetzel, J.I. Brauman, Chem. Rev. 87 (1987) 607.

[6] J.B. Cumming, P. Kebarle, Can. J. Chem. 78 (1978) 1.

[7] J.E. Bartmess, J.A. Scott, R.T. McIver Jr., J. Am. Chem. Soc. 101 (1979) 6046.

[8] J.E. Bartmess, J. Phys. Chem. 98 (1994) 6420.

[9] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney, R.L. Nuttall, J. Phys. Chem. Ref. Data 11 (1982) (suppl).

[10] S.G. Lias, P. Ausloos, J. Am. Chem. Soc. 100 (1978) 6027.

[11] S.W. Benson, Thermochemical Kinetics, 2nd ed., Wiley, New York, 1976.

[12] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Kieth, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. DeFrees, J. Baker, J.J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN 94, Revision C.3, Gaussian Inc., Pittsburgh, PA, 1995.

[13] J.A. Pople, J.S. Binkley, R. Seeger, Int. J. Quantum Chem. 10 (1975) 1.

[14] (a) J.A. Pople, R. Krishnan, H.B. Schlegel, J.S. Binkley, Int. J. Quantum Chem. 13 (1979) 325; (b) K.S. Pitzer, Quantum Chemistry, Prentice Hall, Englewood Cliffs, NJ, 1961.

[15] W.J. Hehre, L. Radom, P.V.R. Schleyer, J.A. Pople, Ab Initio Molecular Theory, Wiley, New York, 1986.

[16] QCPE 455, Quantum Chemistry Program Exchange, Indiana Univ., Bloomington, IN 47405.

[17] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.P.J. Stewart, J. Am. Chem. Soc. 107 (1985) 3902.

[18] M.J.S. Dewar, K.M. Dieter, J. Am. Chem. Soc. 108 (1986) 8075.

[19] J.E. Bartmess, Mass Spectrom. Rev. 8 (1989) 297.

[20] L.V. Gurvich, I.V. Veyts, C.B. Alcock, Thermodynamic Properties of Individual Substances, 4th ed., Hemisphere, New York, 1989, Vol. 1.

[21] The uncertainty in the acidity is the rms average of those for the EA and the BDE.

[22] K.R. Lykke, K.K. Murray, W.C. Lineberger, Phys. Rev. A 43 (1991) 6104.

[23] D. Hanstorp, M. Gustafsson, J. Phys. B 25 (1992) 1773.

[24] P.A. Schulz, R.D. Mead, P.L. Jones, W.C. Lineberger, J. Chem. Phys. 77 (1982) 1153.

[25] C. Blondel, P. Cacciani, C. Delsart, R. Trainham, Phys. Rev. A 40 (1989) 3698.

[26] R. Trainham, G.D. Fletcher, D.J. Larson, J. Phys. B 20 (1987) L777.

[27] R.C. Stoneman, D.J. Larson, J. Phys. B 19 (1986) L405.

[28] J. Berkowitz, G.B. Ellison, D. Gutman, J. Phys. Chem. 98 (1994) 2744.

[29] K.M. Ervin, J. Ho, W.C. Lineberger, J. Phys. Chem. 92 (1988) 5405.

[30] K.K. Murray, T.M. Miller, D.G. Leopold, W.C. Lineberger, J. Chem. Phys. 84 (1986) 2520.

[31] G.K. Moortgart, W. Seiler, P. Warnek, J. Chem. Phys. 78 (1983) 1185.

[32] G.B. Ellison, P.C. Engelking, W.C. Lineberger, J. Am. Chem. Soc. 100 (1978) 2556.

[33] J.A. Seetula, J.J. Russell, D. Gutman, J. Am. Chem. Soc. 112 (1990) 1347.

[34] M.R. Nimlos, G.B. Ellison, J. Am. Chem. Soc. 108 (1986) 6522.

[35] J.A. Seetula, Y. Feng, D. Gutman, P.W. Seakins, M.J. Pilling, J. Phys. Chem. 95 (1991) 1658.

[36] M.R. Nimlos, J.A. Soderquist, G.B. Ellison, J. Am. Chem. Soc. 111 (1989) 7675.

[37] D.F. McMillen, D.M. Golden, Ann. Rev. Phys. Chem. 33 (1982) 493.

[38] F. Breyer, P. Frey, H. Hotop, Z. Phys. A 300 (1981) 7.

[39] R.S. Celotta, R.A. Bennett, J.L. Hall, J. Chem. Phys. 60 (1974) 1740.

[40] T.T. Dang, E.L. Motell, M.J. Travers, E.P. Clifford, G.B. Ellison, C.H. Depuy, V.M. Bierbaum, Int. J. Mass Spectrom. Ion Processes 123 (1993) 171.

[41] R.F. Gunion, M.K. Gilles, M.L. Polak, W.C. Lineberger, Int. J. Mass Spectrom. Ion Processes 117 (1992) 601.

[42] S.E. Bradforth, E.H. Kim, D.W. Arnold, D.M. Neumark, J. Chem. Phys. 98 (1993) 800.

[43] B. Ruscic, J. Berkowitz, J. Chem. Phys. 101 (1994) 7975.

[44] P.C. Engleking, G.B. Ellison, W.C. Lineberger, J. Chem. Phys. 69 (1978) 1826.

[45] A.H. Zimmerman, R. Gygax, J.I. Brauman, J. Am. Chem. Soc. 100 (1978) 5595.

[46] K.B. Clark, P.N. Culshaw, D. Griller, F.P. Lossing, J.A. Martinho Simoes, J.C. Walton, J. Org. Chem. 56 (1991) 5535.

[47] G.B. Ellison, P.C. Engleking, W.C. Lineberger, J. Phys. Chem. 86 (1982) 4873.

[48] P.C. Engelking, W.C. Lineberger, J. Chem. Phys. 67 (1977) 1412.

[49] S. Furuyama, D.M. Golden, S.W. Benson, Int. J. Chem. Kinet. 3 (1971) 237.

[50] P.G. Wenthold, M.L. Polak, W.C. Lineberger, J. Phys. Chem. 100 (1996) 6920.

[51] M. Rossi, D.M. Golden, J. Am. Chem. Soc. 101 (1979) 1230.

[52] S. Moran, G.B. Ellison, J. Phys. Chem. 92 (1988) 1794.

[53] L.G.S. Shum, S.W. Benson, Int. J. Chem. Kinet. 17 (1985) 277.

[54] P.F. Zittel, W.C. Lineberger, J. Chem. Phys. 65 (1976) 1236.

[55] J.H. Richardson, L.M. Stephenson, J.I. Brauman, J. Am. Chem. Soc. 97 (1975) 2967.

[56] F.G. Bordwell, X.M. Zhang, A.V. Satish, J.P. Cheng, J. Am. Chem. Soc. 116 (1994) 6605.

[57] B.K. Janousek, A.H. Zimmerman, K.J. Reed, J.I. Brauman, J. Am. Chem. Soc. 100 (1978) 6142.

[58] E.P. Clifford, P.G. Wenthold, R. Gareyev, W.C. Lineberger, C.H. DePuy, V.M. Bierbaum, G.B. Ellison, J. Chem. Phys. 109 (1998) 10 293.

[59] S.G. Lias, P. Ausloos, Int. J. Mass Spectrom. Ion Phys. 23 (1977) 273.

[60] M.S. Robinson, M.L. Polak, V.M. Bierbaum, C.H. DePuy, W.C. Lineberger, J. Am. Chem. Soc. 117 (1995) 6766.

[61] L.G.S. Shum, S.W. Benson, Int. J. Chem. Kinet. 15 (1983) 433.

[62] A.J. Colussi, F. Zabel, S.W. Benson, Int. J. Chem. Kinet. 9 (1977) 161.

[63] D.M. Wetzel, J.I. Brauman, J. Am. Chem. Soc. 110 (1988) 8333.

[64] R. Walsh, Acc. Chem. Res. 14 (1981) 246.

[65] A.H. Zimmerman, K.J. Reed, J.I. Brauman, J. Am. Chem. Soc. 99 (1977) 7203.

[66] F.G. Bordwell, J.-P. Cheng, G.-Z. Ji, A.V. Satish, X. Zhang, J. Am. Chem. Soc. 113 (1991) 9790.

[67] E. Illenberger, P. Comita, J.I. Brauman, H.-P. Fenzlaff, M. Heni, N. Heinrich, W. Koch, G. Frenking, Ber. Bunsenges Phys. Chem. 89 (1985) 1026.

[68] F.G. Bordwell, J.A. Harrelson Jr., Can. J. Chem. 68 (1990) 1714.

[69] J.L. Holmes, F.P. Lossing, P.M. Mayer, J. Am. Chem. Soc. 113 (1991) 9723.

[70] J.H. Richardson, L.M. Stephenson, J.I. Brauman, Chem. Phys. Lett. 30 (1975) 17.

[71] E.A. Brinkman, K. Salomon, W. Tumas, J.I. Brauman, J. Am. Chem. Soc. 117 (1995) 4905.

[72] A.M. Doncaster, R. Walsh, J. Chem. Soc. Chem. Commun. (1977) 446.

[73] K.J. Reed, J.I. Brauman, J. Chem. Phys. 61 (1974) 4830.

[74] P.N. Noble, R. Walsh, Int. J. Chem. Kinet. 15 (1983) 547.

[75] W. von E. Doering, K. Sarma, J. Am. Chem. Soc. 114 (1992) 6037.

[76] B. Ruscic, J. Berkowitz, J. Chem. Phys. 100 (1994) 4498.

[77] R. Gygax, H.L. Peters, J.I. Brauman, J. Am. Chem. Soc. 101 (1979) 2567.

[78] M.J. Bausch, R. Gotowski, G. Jirka, D. Selmarten, G. Winter, J. Org. Chem. 55 (1990) 5805.

[79] C.B. Freidhoff, J.T. Snodgrass, J.V. Coe, K.M. McHugh, K.H. Bowen, J. Chem. Phys. 84 (1986) 1051.

[80] T. Balkis, A.F. Gaines, G. Ozgen, I.T. Ozgen, M.C. Flowers, J. Chem. Soc., Faraday Trans. 2 72 (1978) 1276.