The gas-phase acidities of the elemental hydrides are functions of electronegativity and bond length[1]

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Abstract: The gas-phase Brønsted acidities of the group 1, group 2, and main group elemental hydrides (XH_n) are shown to be a combined function of the bond length, electronegativity, and position in the periodic table, via a separation of the acidity into coulombic and electronic reorganization enthalpy parts. The Coulombic acidity is defined as the enthalpy to separate unit positive and negative charges from the neutral acid's X—H bond length to infinity; the reorganization enthalpy is the difference between that and the measured acidity, and represents the enthalpy required to reorganize the electrons of the neutral acid, creating an ion pair at the original bond distance. Predictions are made for the gas-phase Brønsted acidities of several elemental hydrides for which this quantity is not known.

Key words: acidity, gas phase, coulomb, elements, hydride.

Résumé : On démontre que les acidités de Brønsted des hydrures de formule générale XH_n des éléments du groupe 1, du groupe 2 et du groupe principal sont une fonction qui combine la longueur de liaison, l'électronégativité et la position dans le tableau périodique par le biais d'une séparation de l'acidité en deux parties impliquant des enthalpies de réorganisation coulombique et électronique. L'acidité coulombique est définie comme l'enthalpie qui sépare une unité de charges positive et négative de la liaison X—H d'un acide neutre de la longueur de liaison jusqu'à l'infini; l'enthalpie de réorganisation est la différence entre ceci et l'acidité mesurée et elle représente l'enthalpie nécessaire pour réorganiser les électrons de l'acide neutre en créant une paire d'ions à la distance originale de la liaison. On fait des prédictions relatives aux acidités de Brønsted de plusieurs hydrures d'éléments pour lesquels cette valeur n'est pas connue.

Mots clés : acidité, phase gazeuse, coulomb, éléments, hydrure.

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Gas-phase acidities of neutral species have traditionally been analyzed in terms of (and the values often obtained from) the thermochemical cycle of Scheme 1, involving the homolytic bond dissociation enthalpy of the generic acid AH, the electron affinity of $A^{\cdot}$, and the ionization energy of the hydrogen atom (1). This cycle has been used to explain observed variations in the acidities of the main group elemental hydrides, wherein the electron affinity is the principal factor in determining the acidities across a row of the periodic table, and the bond dissociation energy the major factor determining the acidities down a column (2).

$$[1] \qquad \Delta_{\mathrm{acid}}H(\mathrm{AH}) = \mathrm{BDE(A\text{-}H)} + \mathrm{IE(H^{\cdot})} - \mathrm{EA(A^{\cdot})}$$

Although Scheme 1 is mathematically rigorous, chemical intuition suggests that there should be some relationship between acidities and electronegativity, and thus perhaps a different method of deriving such acidities. We present here an empirical alternative, using only the relatively low-level quantities of bond lengths, electronegativities, and position in the periodic table. The Coulombic acidity, $\Delta_{\mathrm{CA}}H(\mathrm{AH})$, is here defined as the absolute value of the enthalpy change for separating the acidic proton of an acid AH from its anionic conjugate base A^-, from the distance corresponding to the A—H bond length in the neutral acid to infinity, without any electronic reorganization. This then would be a measure of the gas-phase acidity if only Coulombic forces were involved (3). Coulomb's law along with the necessary physical constants (4) yields:

$$[2] \qquad \Delta_{\mathrm{CA}}H(\mathrm{AH}) = 332.1/d(\mathrm{A—H}) + RT$$

where the Coulombic acidity, $\Delta_{\mathrm{CA}}H(\mathrm{AH})$, is in units of kcal/mol (1 cal = 4.184 J) and the bond length d(A—H) is in angstroms. The constant 332.1 kcal-Å/mol represents the Coulombic acidity at T = 0 K for a standard 1.0 Å bond. This falls in the middle of the scale of known gas-phase ΔH_{acid} values, which range from 294 kcal/mol for $(n\mathrm{C_4F_9SO_2})_2\mathrm{NH}$ to 420 kcal/mol for ethane (5).

If $\Delta_{\mathrm{CA}}H(\mathrm{AH})$ is subtracted from the measured or calculated enthalpy of acidity, $\Delta_{\mathrm{acid}}H(\mathrm{AH})$, defined by Scheme 1 (5), the resulting electronic reorganization enthalpy ($\Delta_{\mathrm{ER}}H$, eq. [3]) represents the energetics of creating the A^-H^+ pair of ions, without having to pay the enthalpy

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This paper is in honor of Professor Paul Kebarle, whose body of research has influenced almost all of JEB's own efforts.

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Scheme 1.

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

$$\Delta_{\mathrm{acid}}H(\mathrm{AH}) = \mathrm{BDE(A\text{-}H)} + \mathrm{IE}(\mathrm{H}^{\cdot}) - \mathrm{EA}(\mathrm{A}^{\cdot})$$

$$[3] \qquad \Delta_{\mathrm{ER}}H(\mathrm{A\text{-}H}) = \Delta_{\mathrm{acid}}H(\mathrm{AH}) - \Delta_{\mathrm{CA}}H(\mathrm{AH})$$

price for separating them so that they do not influence each other's structure via their electric field. It also can be taken as the energy to relax both the atomic and electronic structures (save for the departed proton) from those in the acid to those in the anion.

Experimental data and calculations

Values of experimental bond lengths for the elemental hydrides were compiled from standard sources (6–10). Equilibrium bond lengths (r_e) were the selected ones; when only r_0 values were available, notably for the group 14 hydrides, the r_e values were estimated to be 0.01 Å shorter than the r_0 value. This is consistent with experimental data for H_2, NH_3, H_2O, HCl, PH_3, and H_2Se (6, 10), and with computational approaches (10, 11). For the third through fifth rows, many experimental values were either absent or of considerable uncertainty. The only available experimental bond length for CaH_2, for example, is from a crystal structure, and that is the average of two disparate values in the crystal. For use in the estimation of these missing values, bond lengths obtained from a variety of computational methods are also presented in Table 1. The Gaussian 98 (12) program was utilized, with some of the basis sets taken from the online compilation (13).

It has been noted that correlated computational methods tend to consistently give bond lengths that are longer than those found experimentally, especially for X—H bonds (14–17). As seen in Table 1, for the elemental hydrides under consideration here, the MP2(full)/6-31G(d) geometries used in the Gn methods (18) deviate from experimental values almost exclusively in the direction of being too long. Highly electronegative or electropositive elements seem to deviate the most from agreement, with the alkali metal hydrides being the worst. For the compounds shown, the rms deviation is 0.024 Å. The worst case, KH at 0.075 Å too long, yields a $\Delta_{CA}H$ 5 kcal/mol numerically smaller than that from the experimental bond length. If this trend holds true for the various computational geometries used from the literature, the theoretical ΔH_{ER} values will be slightly too large.

In Table 1, the values overall closest to the experimental ones are from the B3LYP/6-311G(3df,3pd) calculations. These are used to estimate missing experimental values for the first three rows. The 3-21G** basis set, although likely too small for accuracy in itself, is included because it extends to elements in the fourth row, and thus can be used as guidance for estimations there. Computational values for bond lengths of fifth row elements are from a variety of methods in the literature, and from a basis set with the heavy atom modeled with (or using) the CRENBL ECP basis set and pseudopotential (13) and the hydrogen as 3-21G**. This latter choice is also carried through for the fourth row elements, where it is found to deviate by less than 0.05 Å from experimental bond lengths for the main group elements. Gas-phase enthalpies of acidity were obtained via Scheme 1, save that a few were from equilibrium data anchored to values from Scheme 1 (5). Again, there are a number of elemental hydrides for which experimental $\Delta_{\mathrm{acid}}H$ values are not available. For MgH_2 and AlH_3, we have computed $\Delta_{\mathrm{acid}}H(\mathrm{AH})$ at $T = 298$ K from a series of ab initio CCSD(T)/aug-cc-pVxZ calculations (x = D, T, Q), which are then extrapolated to the complete basis set limit (19). For HF, HCl, H_2O, and H_2S, this method of computation reproduces the experimentally obtained acidities to within 0.5 kcal/mol, comparable to the experimental error (19).

From the data for these quantities given in Tables 1 and 2, values of $\Delta_{CA}H$ and $\Delta_{ER}H$ are derived as per eqs. [2] and [3]. To examine the generality of the concepts developed here, we have also examined the corresponding experimental and computational data for the elemental monohydrides, as given in Table 3.

Results

The values obtained for $\Delta_{ER}H$ in Table 2 range from 9 kcal/mol for FH to 211 kcal/mol for CsH, with an anomalous value of –48 kcal/mol for H_2 (which is discussed separately in the following). Are these values of a reasonable magnitude? Gas-phase basicities likewise involve loss of a proton with no Coulombic cost of charge separation (rxn. [4]), only the energetics of bond breaking. That experimental basicity scale ranges from 42.5 kcal/mol for He (giving HeH^+) to 248 kcal/mol for NaOH (5). The magnitudes of the values obtained for the reorganization enthalpies are thus reasonable in this light.

$$[4] \qquad \mathrm{BH}^{+} \rightarrow \mathrm{B} + \mathrm{H}^{+}$$

Examination of the $\Delta_{ER}H$ values in Table 2 reveals a distinct periodic trend: $\Delta_{ER}H$ decreases across a row of the periodic table, and increases down a column. The smallest positive $\Delta_{ER}H$ is for HF. This is reasonable in that HF is the elemental hydride with the largest difference in electronegativity between the hydrogen and the heavy atom. The electrons in HF are thus already well on the way to being reorganized toward the products of F^- and H^+, and relatively little further reorganization is necessary. The other extreme, of very large $\Delta_{ER}H$ values for the alkali hydrides, reflect the opposite polarization of charge. Considerable energy is required to move electrons to an electropositive element.

The negative $\Delta_{ER}H$ for H_2 appears anomalous. The Coulombic acidity of H_2 is the weakest in Table 2, weaker even than the experimental acidity, owing to the very short bond length engendered by the 1s—1s bonding in H_2. The negative $\Delta_{ER}H$ in this case would seem to imply that H_2 should exist as H^-H^+ rather than H—H at the equilibrium bond length, a situation clearly at odds with observations. However, it has been noted (20) that the H—H bond requires

Table 1. Bond lengths (in angstroms) of elemental hydrides.

	d(A—H)[a]							
Acid	Exptl.	MP2(fu)/6-31G(d)	MP2(fu)/3-21G**	B3LYP/3-21G**	B3LYP/6-311G**(3df,3pd)	B3LYP/6-311G	CCSD(T)/cc-pvtz	Other computational
H_2	0.7414	0.7375	0.7382	0.7464	0.7440	0.7427	0.7427	
LiH	1.5947	1.6396	1.6319	1.6213	1.5930	1.5894	1.6078	
BeH_2	(1.325)	1.3329	1.3313	1.3344	1.3267	1.3250	1.3339	
BH_3	1.1800^b	1.1910	1.1854	1.1949	1.1890	1.1879	1.1914	
CH_4	1.0856^b	1.0894	1.0802	1.0895	1.0907	1.0878	1.0890	
NH_3	1.0118	1.0168	1.0014	1.0123	1.0159	1.0136	1.0140	
OH_2	0.9579	0.9686	0.9506	0.9662	0.9619	0.9603	0.9594	
FH	0.9169	0.9339	0.9138	0.9323	0.9199	0.9186	0.9170	
NaH	1.8874	1.9181	1.8963	1.8640	1.8870	1.8752	1.9232	
MgH_2	(1.700)	1.7213	1.7109	1.7110	1.7042	1.7010	1.7116	
AlH_3	(1.581)	1.5888	1.5811	1.5935	1.5831	1.5790	1.5853	
SiH_4	1.4711^b	1.4825	1.4756	1.4896	1.4839	1.4793	1.4831	
PH_3	1.4200	1.4140	1.4062	1.4246	1.4235	1.4179	1.4184	
SH_2	1.3356	1.3395	1.3293	1.3479	1.3480	1.3418	1.3409	
ClH	1.2746	1.2800	1.2674	1.2849	1.2871	1.2808	1.2773	
KH	2.242	2.3178	2.3444	2.3052	2.2436	2.2398		
CaH_2	(2.040)	2.1235	2.1461	2.1335	2.0499	2.0483	2.0879	
GaH_3	(1.560)	1.5762	1.5570	1.5600	1.5672	1.5663	1.5623	1.586^c
GeH_4	1.5151^b	1.5421	1.5219	1.5325	1.5347	1.5334	1.5229	
AsH_3	1.5108	1.5357	1.5119	1.5331	1.5251	1.5240	1.5096	
SeH_2	1.4600	1.4806	1.4567	1.4767	1.4717	1.4697	1.4584	
BrH	1.4144	1.4356	1.4091	1.4260	1.4263	1.4236	1.4131	
RbH	2.367		2.4792	2.4515^d				
SrH_2	(2.2)		2.3206	2.3056^d				2.201^c
InH_3	(1.7)		1.7623	1.7854^d				1.734^e
SnH_4	1.7008^b		1.7314	1.7497^d				
SbH_3	1.7039		1.7196	1.7482^d				
TeH_2	1.658		1.6690	1.6901^d				
IH	1.6092		1.6235	1.6416^d				
CsH	2.4938			2.5211^d				
BaH_2	(2.1)			2.2923^d				2.314^c
TlH_3	(1.76)			1.8368^d				1.756^e
PbH_4	(1.77)			1.8400^d				1.767^e
BiH_3	(1.82)			1.8897^d				1.826^e
PoH_2	(1.73)			1.7896^d				1.835^f
AtH								
C_2H_4	1.0760	1.0826						
HC≡CH	1.0550	1.0618						

[a] Experimental bond lengths (6–9). Values in parentheses are estimated from computational values as per the text.

[b] Estimated r_e value by reducing the r_0 value by 0.01 Å.

[c] Reference 34.

[d] H is stated basis set; heavy atom is CRENBL ECP basis set and pseudopotential (13).

[e] Reference 35, QCI calculations.

[f] Reference 36, second-order CI/CASSCF calculations.

about a 5% ionic contribution to the "pure" covalent bond predicted by electronegativity to explain the bond length and enthalpy; this may be the reason for this unusual result. In addition, a plot of the homolytic bond dissociation energies of the elemental hydrides (5) against the reciprocal of the X—H bond length yields a moderately linear (r = 0.96, sd = 8.4 kcal/mol) correlation, with H_2 as an outlier. Its bond dissociation energy is 62 kcal/mol stronger than expected from its bond length. One additional possibility is that the electronegativity value is not applicable in this case, although it would require an X of <1.94 or a bond length of >0.84 Å to make $\Delta_{ER}H$ (H_2) positive. We emphasize that this "anomalous" $\Delta_{ER}H$ is really a problem with the $\Delta_{CA}H$ being too weak, not the $\Delta_{ER}H$ being too strong.

Table 2. Coulombic acidity and electron reorganization enthalpy of elemental hydrides.

Acid	$\Delta_{CA}H^{a}$	$\Delta_{acid}H^{b}$	$\Delta_{acid}H^{c}$	$\Delta_{ER}H^{d}$	$X_{A}{}^{e}$
H_2	448.5	400.4±0.01	*406.7*	–48.1	2.25
LiH	208.7	356.0±0.1	*348.8*	147.3	0.97
BeH_2	*251.2*	387.4±3.0	*389.8*	136.2	1.54
BH_3	282.0	*411.8*^{f}	*411.3*	*129.8*	2.04
CH_4	307.0	416.7±0.8	*417.3*	109.7	2.48
NH_3	328.9	404.3±0.3	*403.0*	75.4	3.04
OH_2	347.1	390.7±0.1	*390.1*	43.6	3.68
FH	362.8	371.6±0.2	*371.4*	8.8	4.30
NaH	176.6	345.1±0.3	*340.2*	168.6	0.91
MgH_2	*195.9*	360.7±2.4	*361.1*	*164.8*	1.37
AlH_3	*210.8*	*373.2*^{f}	*371.4*	*162.4*	1.83
SiH_4	226.3	372.8±0.8	*372.2*	146.5	2.28
PH_3	236.1	363.7±1.6	*365.8*	127.6	2.41
SH_2	249.2	350.7±0.9	*350.1*	101.5	2.86
ClH	261.1	333.4±0.01	*332.3*	72.3	3.34
KH	148.7	344.4±5.0	*339.2*	195.7	0.73
CaH_2	*162.2*	353.1^{c}	*353.1*	*190.9*	1.08
GaH_3	*211.2*	*367.2*^{c}	*367.2*	*156*	2.01
GeH_4	219.8	358.9±1.3	*362.9*	139.1	2.33
AsH_3	220.4	357.5±2.1	*359.6*	137.1	2.38
SeH_2	228.1	341.5±0.7	*342.6*	113.4	2.79
BrH	235.4	323.5±0.05	*324.7*	88.1	3.20
RbH	140.9	343.4±0.5		202.5	0.69
SrH_2	*152*	*354*		*202*^{g}	1.00
InH_3	*196*	*384*^{h}		*183*^{g}	1.76
SnH_4	195.9	350.5±2.1		154.7	2.21
SbH_3	195.5	*349*^{h}		154^{g}	2.22
TeH_2	200.9	331.1±1.1		130.2	2.57
IH	207	314.3±0.02		107.3	2.95
CsH	133.8	344.6±0.1		210.8	0.62
BaH_2	*159*	*375*^{h}		*216*^{g}	0.88
TlH_3	*189*	*364*^{h}		*175*^{g}	1.96
PbH_4	*188*	*333*^{h}		*145*^{g}	2.41
BiH_3	*183*	*337*^{h}		*154*^{g}	2.28
PoH_2	*193*	*323*^{h}		*130*^{g}	2.65
AtH	—	—		*104*^{g}	3.05
$CH_2{=}CH_2$	315.4	409.4		94.0	2.73^{i}
HC≡CH	307.2	378.0		70.8	3.16^{i}

Note: Values in italics are derived wholly or in part from ab initio computations and the correlations described in the text. All energetics are kcal/mol at 298 K.

[a] Coulombic acidity from eq. [2].

[b] Experimental enthalpy of acidity (5).

[c] G3(MP2) enthalpy of acidity.

[d] Electron reorganization enthalpy (eq. [3]).

[e] Mulliken–Jaffé electronegativity (23).

[f] ΔH_{acid} (BH_3) is calculated at the B3LYP/aug-cc-pVTZ level as per ref. 19. The triplet ground state for BH_2^- is used; the singlet is calculated as 0.7 kcal/mol higher in energy.

[g] Extrapolated from X_A with eqs. [6]–[10]; up to ±10 kcal/mol uncertain.

[h] Unknown experimentally. Value is from eq. [2] combined with eqs. [6]–[10].

[i] Calculated from an inversion of eq. [6].

Table 3. Coulombic acidity and electron reorganization enthalpy of elemental monohydrides.

Acid	d(A—H)^{a}	$\Delta_{CA}H^{b}$	$\Delta_{acid}H^{c}$	$\Delta_{ER}H^{d}$	$\Delta_{promo}H^{e}$
H_2	0.7414	448.5	400.4	–48.1	
LiH	1.5947	208.9	356	147.1	
BeH	1.3426	248.0	*371.5*^{f}	*123.5*	
BH	1.2324	270.1	387.7	117.6	8.7
CH	1.1199	297.1	365.1	68.0	28.4
NH	1.0362	321.1	*404.9*^{f}	*83.8*	
OH	0.9677	343.8	382.6	38.8	
FH	0.9169	362.8	371.3	8.5	
NaH	1.8874	176.6	345.1	168.5	
MgH	1.7297	192.6	*350.0*^{f}	*157.4*	
AlH	1.6478	202.1	371.7	169.6	7.7
SiH	1.5201	219.1	353.1	134.0	19.9
PH	1.4223	234.1	367.7	133.6	
SH	1.3409	248.3	350.4	102.1	
ClH	1.2746	261.2	333.4	72.2	
KH	2.2420	148.7	344.1	195.4	
CaH	2.0025	166.4	352.8	186.4	
GaH	1.6630	200.3	369.6	169.3	5.7
GeH	1.5880	209.7	348.3	138.6	19.2
AsH	1.5394	216.3	359.4	143.1	
SeH	1.4750	225.8	339.9	114.1	
BrH	1.4144	235.4	323.5	88.1	
RbH	2.3670	140.9	343.4	202.5	
SrH	2.1456	155.4	350.5	195.1	
InH	1.838	181.3	362.5	181.2	
SnH	1.8215	182.9	343.0	160.1	16.5
SbH	1.7226	193.4	345.1	151.7	
TeH	1.741	191.4	333.2	141.8	
IH	1.6092	207.0	314.3	107.3	
CsH	2.4938	133.8	344.6	210.8	
BaH	2.2318	149.4			
TlH	1.87	178.2	351.3	173.1	
PbH	1.8388	181.2	347.5	166.3	
BiH	1.805	184.6			

[a] Experimental bond lengths in angstroms (6).

[b] Coulombic acidity from eq. [2] (kcal/mol).

[c] Experimental enthalpy of acidity (kcal/mol) (5).

[d] Electronic reorganization enthalpy (kcal/mol, eq. [3]).

[e] Term energy for first excited state of the atomic anion corresponding to the multiplicity of the monohydride acid.

[f] Anion unbound; acidity is from G3(MP2) calculations.

If the $\Delta_{ER}H$ values are plotted as a function of the Mulliken–Jaffé electronegativity (21–23), the main group hydrides and the alkali metal hydrides yield excellent (r = 0.979 and 0.999, respectively) correlations, as shown in Fig. 1. This electronegativity scale is based on the equation of Mulliken (21), involving ionization energies and electron affinities, but with more recent values of those quantities used to obtain the numeric electronegativity, and separate values for different hybridization states (23). For the main group compounds with eight valence electrons:

$$[5] \qquad \Delta_{ER}H(AH) = -67.2 \times X_A + 295.6 \text{ kcal/mol}$$

$$r = -0.9778$$

where X_A is the Mulliken–Jaffé electronegativity of atom A (23). The largest deviation from eq. [5] is that of methane at 19 kcal/mol, and the average deviation is 8.2 kcal/mol. Other electronegativity scales, such as the Allred–Rochow (24), Sanderson (25), and Pauling (20) scales, yield similar,

Fig. 1. Electronic reorganization enthalpy (kcal/mol) vs. Mulliken–Jaffé electronegativity, all elemental hydrides. Lines are least-squares fit to a row or column.

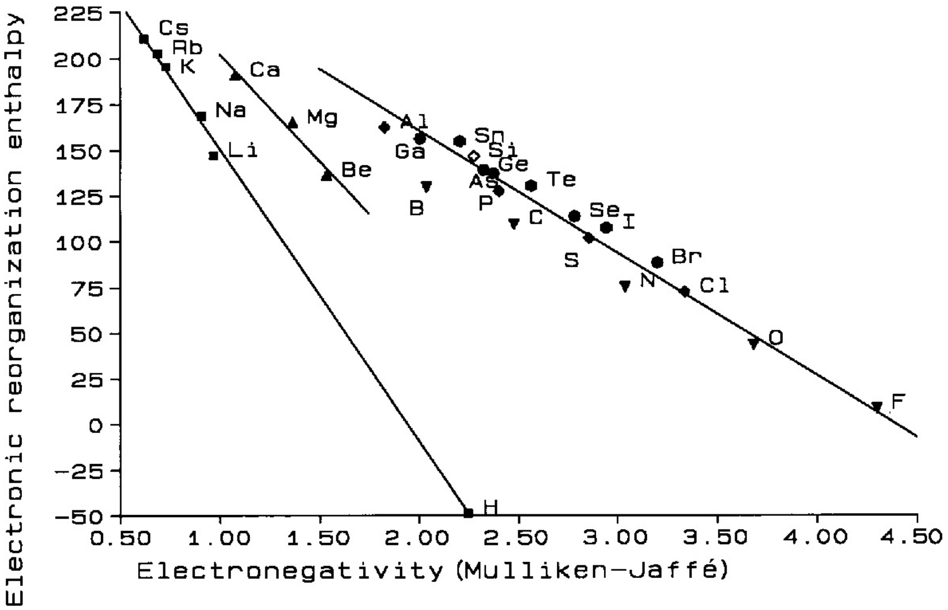
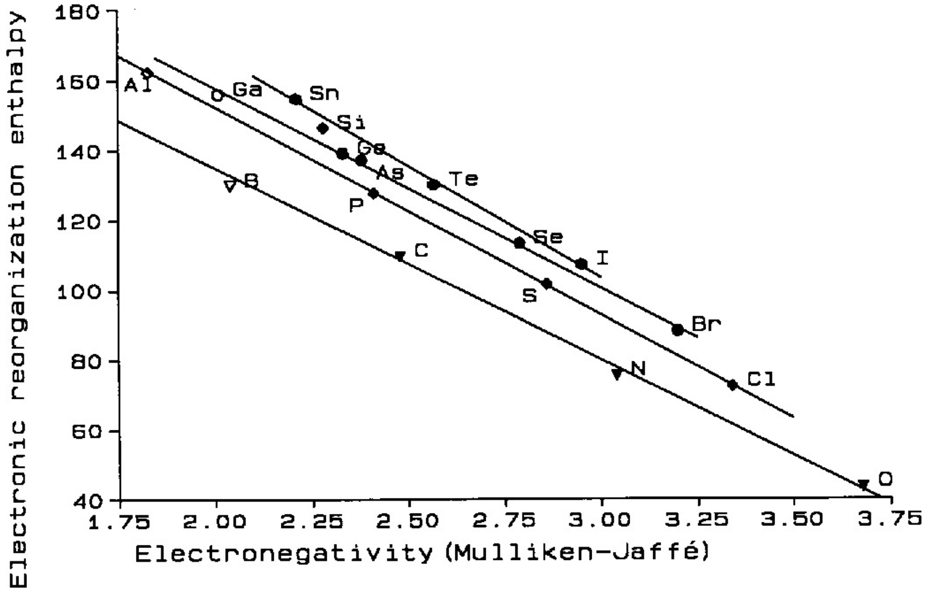


Fig. 2. Electronic reorganization enthalpy (kcal/mol) vs. Mulliken–Jaffé electronegativity for the main-group hydrides. Lines are least-squares fit to a row. Open symbols are in part computational and are not included in the least-squares fit. Fluorine is on the first row line, but off-scale for reasons of legibility.



though not quite as good, correlations, with r values of 0.95 or higher.

Closer examination of the main group compounds (shown in Fig. 2) reveals that the correlation between $\Delta_{ER}H$ and electronegativity X_A is even stronger when each row of the periodic table is considered individually

[6] CH_4 through HF: $\Delta_{ER}H = (-54.8 \pm 1.5) \times X + (244 \pm 5) \qquad r = -0.9992,\ \mathrm{sd} = 1.5$

[7] SiH_4 through HCl: $\Delta_{ER}H = (-68.1 \pm 6.3) \times X + (298 \pm 17) \qquad r = -0.9913,\ \mathrm{sd} = 4.2$

[8] SiH_4 without SiH_4: $\Delta_{ER}H = (-59.5 \pm 0.8) \times X + (271 \pm 2) \qquad r = -0.9999,\ \mathrm{sd} = 0.3$

[9] GeH_4 through HBr: $\Delta_{ER}H = (-63.3 \pm 4.4) \times X + (290 \pm 11) \qquad r = -0.993,\ \mathrm{sd} = 0.6$

[10] SnH_4, TeH_2, HI: $\Delta_{ER}H = (-64.0 \pm 2.2) \times X + (296 \pm 6) \qquad r = -0.9994,\ \mathrm{sd} = 0.7$

where $\Delta_{ER}H$ is in kcal/mol and the correlated data are confined to experimental values.

It is evident that SiH_4 deviates from eq. [8], being 11 kcal/mol more weakly acidic than predicted by this correlation. There is no obvious chemical reason for silane being special. The deviation must lie in the measured geometry, acidity, or electronegativity. The silyl anion and radical are both clearly pyramidal (26), so it is not a matter of using the wrong hybridization state in choosing the electronegativity (23). The experimental bond length agrees with computations. To put the measured $\Delta_{ER}H$ on the line of eq. [8] requires either $X = 2.1$, or a strengthening of the measured acidity by 11 kcal/mol. An error of the latter size seems unlikely, considering the internal consistency of the experimental gas-phase acidity scale (5), and its agreement with the value from Scheme 1 for silane. It is noteworthy, however, that the difference between the Mulliken–Jaffé electronegativity for tetrahedral Si ($X_{Si} = 2.28$) and the Pauling electronegativity for the same element and hybridization state ($X_{Si} = 1.90$) is the greatest for any main group element listed in the Bratsch tables (23). A smaller X_{Si} value would put the silane point closer to the least-squares line.

Both the slopes and intercepts of eqs. [6]–[10] show periodic trends: the acids in rows lower in the periodic table are more sensitive to electronegativity in determining their $\Delta_{ER}H$ value. The intercepts of these equations indicate weaker intrinsic $\Delta_{ER}H$ at zero electronegativity, as one goes lower in the table. Because electronegativity also follows periodic trends, this implies that perhaps a somewhat higher power function might be more applicable. However, we believe that the precision of both the experimental data and the electronegativities does not support further extension of this.

In contrast, the alkali metal hydrides (and hydrogen), with two valence electrons, fall on a separate line from the main group elements, and $\Delta_{ER}H$ is stronger than expected relative to the main group. Proton loss for these group 1 hydrides involves an s orbital, as opposed to the p shell of the main group species, so a different correlation is not surprising. The group 2 acids BeH_2, MgH_2, and CaH_2 fall between the group 1 and main group lines. It is therefore clear that orbital occupation is another variable that affects the gas-phase acidities of the elemental hydrides. The greater sensitivity of $\Delta_{ER}H$ of the group 1 and 2 acids to electronegativity than for the main group species, may reflect the proximity of the bonding s orbital to the nucleus, compared with the participation of the more distant p electrons for the main group elements.

There are several elemental hydrides for which the experimental gas-phase acidity is not known and for which reliable computational approaches fail because the necessary basis sets are unavailable, or because relativistic effects are important. Using eq. [3] in combination with eqs. [2] and [7], [9], or [10] yields predictions in Table 2 for these unknown gas-phase acidities including those of SrH_2, InH_3, SbH_3, and the row 5 species BaH_2, TlH_3, PbH_4, BiH_3, and PoH_2. Because of the uncertainty in even the order of bond length in the row 5 acids, as noted earlier, the derived acidities are expected to be uncertain by at least ±10 kcal/mol.

Likewise, a rearrangement of eqs. [2] and [5] allows prediction of an effective group electronegativity for hydrocarbon fragments from known bond lengths and gas-phase acidities. For -CH=CH_2 and $\text{-C}\equiv\text{CH}$, as seen in Table 2, derived electronegativities of 2.73 and 3.16, respectively, are obtained. The first value is somewhat larger than that of the sp^3 carbon at 2.48, but the value for $\text{-C}\equiv\text{CH}$ places the electronegativity of an sp carbon between that of N and O, as expected (27). From the Pauling definition of electronegativity in eq. [11], we can utilize currently available

$$[11]\quad |X_A - X_B| = 0.208[D(\text{A—B}) - D(\text{A—A}) + D(\text{B—B})/2]^{1/2}$$

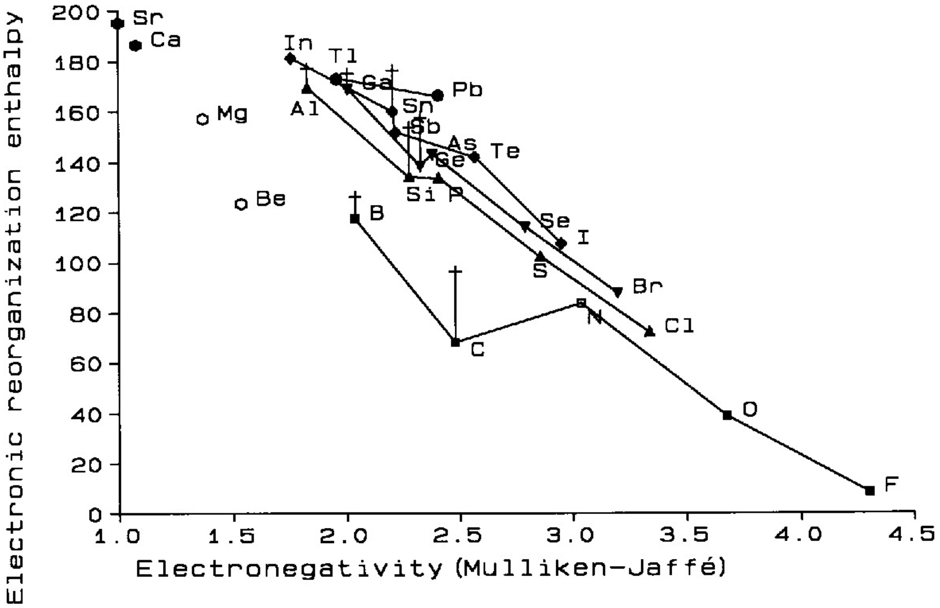
thermochemistry (5) to obtain Pauling electronegativities for the groups $\text{-CH}_2\text{CH}_3$, -CH=CH_2, and $\text{-C}\equiv\text{CH}$ of 2.56, 2.58, and 2.93, respectively, relative to $X_F = 4.0$ (28). Wells (29) reports group electronegativities for these of 2.3, 3.0, and 3.3, but the derivation of these values is not clear. Taft and co-workers (30) give polar σ values of 0.16, 0.17, and 0.28 for the groups based on calculated charge densities on the acidic hydrogen in the acids, implying again that ethenyl is only slightly more electronegative than ethyl, but ethynyl considerably more so. Boyd and Boyd (31) present group electronegativity values of 2.55, 2.58, and 2.66. The Mulliken–Jaffé electronegativities (23) for these hybridization states are 2.48, 2.66, and 2.99, relative to $X_F = 4.30$. Guillermin et al. (32) likewise comment on these points.

For the elemental monohydrides (in Table 3 and Fig. 3), it is evident that while there is a general correlation with electronegativity, there is considerably more scatter here than for the saturated hydrides. A complicating factor with these monohydride acidities is that the most thermochemically stable monohydride acid and atomic conjugate base can have different spin states, i.e., CH is a ground-state doublet while C^- is a quartet, with the anion doublet state 28 kcal/mol higher in energy. The group 13 and 14 monohydrides are all such cases. Such a multiplicity change during a proton transfer can result in an appreciable barrier and a concomitant lack of reactivity (34). Also, several of the atomic anions (N^-, Be^-, Mg^-) are not bound with respect to electron loss; values for these are obtained computationally at the G3(MP2) (18) level, and are shown as open symbols in Fig. 3. Finally, the electronegativities used here are hybridization state dependent (23), and it is not clear whether the hybridization of the acid or conjugate base should be used. We thus take Fig. 3 as indicating semiquantitative agreement at best with the general concept presented here. The monohydride $\Delta_{ER}H$ values are in general within a few kcal/mol of the saturated hydride ones, save that CH is notably 41 kcal/mol weaker than methane.

This correlation of acidity with bond length and electronegativity is an empirical one, unlike the rigorous thermochemical cycle in Scheme 1. Is there a physical rationale for this? We argue that for a limited series of structurally related compounds, such as the elemental hydrides here, it is not unreasonable that a longer bond should be proportionately weaker, in the homolytic sense. As noted earlier, excluding H_2, this holds to within a standard deviation of 7.1 kcal/mol for these species.

Likewise, the Mulliken definition of electronegativity involves an average of the electron affinity and ionization energy of the species involved. Thus, qualitatively both bond dissociation energies and electron affinities are related to the quantities used here. It appears that there are canceling ef-

Fig. 3. Reorganization enthalpy (kcal/mol) vs. Mulliken–Jaffé electronegativity, all elemental monohydrides. Open symbols denote computational values for unbound anions. Species of a row are connected. Vertical lines to a cross show the effect of promotion of the anion to the same multiplicity state as the acid.



fects in the differences between Scheme 1 and eqs. [2] and [6]–[10].

The gas-phase acidities of sp^3 carbon acids, all of which have the same nominal C—H bond length and electronegativity, are spread across a range of values 122 kcal/mol wide, from ethane to $(C_4F_7SO_2)_2CH_2$ (5). The correlations found here are thus not general ones, but valid only for the elemental hydrides, where the additional effects of resonance, polarity, and polarizability arising from the substituents on the central atom are not present or cancel out. Nevertheless, within this chemically related family of molecules, the gas-hase acidities can be shown to be simply and intuitively related to molecular geometry, atomic electronegativity, and position in the Periodic table.

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References

1. E.C. Baughn. J. Chem. Soc. 1403 (1940).
2. J.I. Brauman and L.K. Blair. J. Am. Chem. Soc. **93**, 3911 (1971).
3. K.E. Laidig and A. Streitwieser, Jr. J. Comp. Chem. **17**, 1771 (1996).
4. E.R. Cohen and B.N. Taylor. J. Res. Nat. Bur. Stand. **92**, 85 (1987).
5. W.G. Mallard and P.J. Linstrom (*Editors*). NIST Chemistry WebBook, NIST Standard Reference Database Number 69 [online]. National Institute of Standards and Technology, Gaithersburg, Md. Available from http://webbook.nist.gov/chemistry/. June 2005.
6. K.P. Huber and G. Herzberg. *In* Molecular spectra and molecular structure. IV. Constants of diatomic molecules. 2nd ed. Van Nostrand Reinhold Co., New York. 1979.
7. K.-H. Hellwege (*Editor*). Landolt–Börnstein numerical data and functional relationships in science and technology II/6: Molecular constants. Springer-Verlag, Berlin. 1974.
8. O. Madelung (*Editor*). Landolt–Börnstein numerical data and functional relationships in science and technology II/15: Structure data of free polyatomic molecules. Springer-Verlag, Berlin. 1987.
9. W. Martienssen (*Editor*). Landolt–Börnstein numerical data and functional relationships in science and technology II/23: Structure data of free polyatomic molecules. Springer-Verlag, Berlin. 1995.
10. M.D. Harmony. Acc. Chem. Res. **25**, 321 (1992).
11. F. Pawlowski, P. Jorgensen, J. Olsen, F. Hegelund, T. Helgaker, J. Gauss, K.L. Bak, and J.F. Stanton. J. Chem. Phys. **116**, 6482 (2002).
12. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, and J.A. Pople. Gaussian 98. Revision A.7 [computer program]. Gaussian, Inc., Pittsburgh, Penn. 1998.
13. Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory (EMSL). Extensible Computational Chemistry Environment Basis Set Database. Version 02/25/04. EMSI Gaussian basis sets [online]. Pacific North-

west Laboratory, Richland, Washington. Available from http://www.emsl.pnl.gov/forms/basisform.html.

14. D. Cremer, E. Kraka, and Y. He. J. Mol. Struct. **567–568**, 275 (2001).
15. Y. He and D.J. Cremer. J. Phys. Chem. A, **104**, 7679 (2000).
16. D. Cremer, A. Wu, A. Larsson, and E. Kraka. J. Mol. Model. **6**, 396 (2000).
17. J. Sánchez Márquez and M. Fernández Núñez. J. Mol. Struct: THEOCHEM, **624**, 239 (2003).
18. L.A. Curtiss, P.C. Redfern, K. Raghavachari, V. Rassolov, and J.A. Pople. J. Chem. Phys. **110**, 4703 (1999).
19. R.J. Hinde. J. Phys. Chem. A, **104**, 7580 (2000).
20. L. Pauling. The nature of the chemical bond. Cornell University Press, Ithaca, N.Y. 1939. Chap. 2.
21. R.S. Mulliken. J. Chem. Phys. **2**, 782 (1934).
22. J. Hinze, M.A. Whitehead, and H.H. Jaffé. J. Am. Chem. Soc. **85**, 148 (1968).
23. S.G. Bratsch. J. Chem. Educ. **65**, 34 (1988).
24. A.L. Allred and E.G. Rochow. J. Inorg. Nucl. Chem. **5**, 264 (1958); **5**, 269 (1958).
25. R.T. Sanderson. J. Am. Chem. Soc. **105**, 2259 (1983).
26. M.R. Nimlos and G.B. Ellison. J. Am. Chem. Soc. **108**, 6522 (1986).
27. A.D. Walsh. Discuss. Faraday Soc. **2**, 18 (1947).
28. The literature experimental value for $\Delta_f H^0$(HC≡CCl) appears to be at least 16 kcal/mol too positive, based on group additivity and G3(MP2) calculations: E. Kloster-Jensen, C. Pascual, and C.J. Vogt. Helv. Chim. Acta, **53**, 2109 (1970).
29. P.R. Wells. Prog. Phys. Org. Chem. **6**, 111 (1968).
30. S. Marriott, W.F. Reynolds, R.W. Taft, and R.D. Topsom. J. Am. Chem. Soc. **106**, 959 (1984).
31. R.J. Boyd and S.L. Boyd. J. Am. Chem. Soc. **114**, 1652 (1992).
32. J.-C. Guillermin, E.H. Ruiague, J.-F. Gal, P.-C. Maria, O. Mó, and M. Yáñez. Chem. Eur. J. **11**, 2145 (2005).
33. G.A. Janaway and J.I. Brauman. J. Phys. Chem. A, **104**, 1795 (2000).
34. M. Kaupp, P.v.R. Schleyer, H. Stoll, and H.J. Preuss. Chem. Phys. **94**, 1360 (1991)
35. P. Schwerdtfeger, G.A. Heath, M. Dolg, and M.A. Bennett. J. Am. Chem. Soc. **114**, 7518 (1992).
36. K. Sumathi and K. Balasubramanian. J. Chem. Phys. **92**, 6604 (1990).