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Some Hazards of Electronegativity Correlations

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The linear correlations of enthalpy of formation differences with electronegativity (covalent potential, V_x), published by Luo and Benson (LB), have been reexamined with inclusion of additional data for silicon and other group 14 organometallic compounds. While there is support for the idea that the covalent potential represents a good scale for such correlations, certain conclusions of LB are not supported. The correlations yield the following $\Delta H_f°$ values (kJ mol^{-1}): SiH_3I, +8.6; Me_3SiF, −586; Me_3SiNH_2, −291; Me_3SiSH, −273, in close agreement with LB. However, there is no case for revision of $\Delta H_f°(Si_2H_6) = 80.0$ kJ mol^{-1} and our estimated $\Delta H_f°$ values (kJ mol^{-1}), for $MeGeH_3$ (42 ± 4) and $MeSnH_3$ (118 ± 4) do not fit the linear correlations previously proposed. It is shown that average hydrogen-for-methyl substitution enthalpies fit best a nonlinear correlation with V_x, just as shown earlier by Benson and co-workers for the same correlation with Pauling electronegativity.

Introduction

During the course of a review of the thermochemistry of organosilicon compounds,[1] we were led to examine some recent attempts at the correlation of thermochemical properties of some of these compounds with the electronegativities of their bonded atoms. This approach originated with Pauling,[2] but the recent work by Luo and Benson[3,4] employs a new scale of electronegativity called "unshielded core potential" or more simply "covalent potential". In a series of papers,[3−11] Luo and Benson have applied the covalent potential, V_x, to the correlation of enthalpies of formation and argued that it is more successful in this exercise than other scales of electronegativity.[11] Some of these have been devoted to organosilicon compounds.[7−10] The correlations appear generally to be good and have been exploited by Luo and Benson[9] to obtain new $\Delta H_f°$ values for Me_3SiF, Me_3SiNH_2, and Me_3SiSH and a revised $\Delta H_f°$ value for SiH_3I. In addition they have suggested[10] a revision of $\Delta H_f°(Si_2H_6)$. These claims have led us to examine the correlations more closely.

Enthalpy of Formation Difference Correlations with V_x

We present here a detailed examination of four of the correlations published by Luo and Benson (LB). In some of them we have added other data not included in the original correlations. We have also represented data points that have significant uncertainties with error bars estimated from the cited experimental uncertainties where possible, to assist readers to judge the significance of deviations from the plots. For the most part we avoid discussing the correlation lines in terms of representational equations since, in our view, equations can often be taken to imply a more accurate linkage between correlated quantities than in fact exists. Although the citation of error limits on gradients and intercepts (not employed by LB[3−11]) in principle would overcome this objection, this can also be deceptive with such equations because usually the standard deviations of slopes and intercepts are highly correlated.

TABLE 1: Enthalpy of Formation Data (kJ mol^{-1})[a] for the Silyl/Hydrogen Compound Difference (Δ_1) Correlation with Electronegativity

X	V_x/(Å)$^{-1}$	$\Delta H_f°(SiH_3X)$	$\Delta H_f°(HX)$	Δ_1	p[b]
F	9.915	−359 ± 8	−273.2 ± 0.8[c]	−85.8 ± 8	1
Cl	7.04	−136 ± 10	−92.3 ± 0.1[c]	−43.7 ± 10	1
Br	6.13	−64 ± 10	−36.3 ± 0.17[c]	−27.7 ± 9	1
I	5.25	−2 ± 8	+26.5 ± 0.13[c]	−28.5 ± 8	1
CH_3	5.19	−29.1 ± 4	−74.5 ± 0.4[d]	+45.4 ± 4	4
SiH_3	3.41	+80.3 ± 1.5	+34.3 ± 1.2	+45.7 ± 1.9	4
H	2.70	+34.3 ± 1.2	0[c]	+34.3 ± 1.2	2

[a] Data taken from ref 1 or 13, unless otherwise stated. [b] See text for definition. [c] From ref 16. [d] From ref 4.

We begin by examining the correlations that involve silyl and trimethylsilyl compounds to evaluate their strengths and weaknesses. This leads us to return to the correlation between methyl and hydrogen compounds, in a further attempt to answer the question, fundamental to organic and organometallic thermochemistry, viz, is there a quantitative way to estimate the enthalpy increment of methyl-for-hydrogen substitution?

(i) $\Delta_1 = [\Delta H_f°(SiH_3X) - \Delta H_f°(HX)]$. The published enthalpy data for this correlation are shown in Table 1. These are essentially those used by LB[8] but with two data points added (see below). Figure 1 shows the correlation between Δ_1 and V_x. The original plot featured X = H, I, Br, Cl, and F. We have added X = SiH_3 and CH_3. The "best fit" line ignores the points we have added. For X = I the fit is clearly not good, and this supports the revision[1,8] of $\Delta H_f°(SiH_3I)$ from −2.0 to +8.6 kJ mol^{-1}. The situation, however is not so simple for for X = H, SiH_3, and CH_3. Plainly these points also do not fit. LB[5,8] argued that the true correlation test requires the use of a parameter, *p* (=the number of interchangeable H atoms in the HX molecule) such that the real correlation should be between Δ_1/p and V_x rather than Δ_1 and V_x. Thus $\Delta_1(X = H) = [\Delta H_f°(SiH_4) - \Delta H_f°(H_2)]$ is divided by 2. This point, also shown in Figure 1 (as X = H′), perfectly fits the correlation line. However, for the points we have added, $\Delta_1(X = SiH_3) = [\Delta H_f°(Si_2H_6) - \Delta H_f°(SiH_4)]$ and $\Delta_1(X = CH_3) = [\Delta H_f°(SiH_3CH_3) - \Delta H_f°(CH_4)]$ should be divided by 4. It can be seen that,

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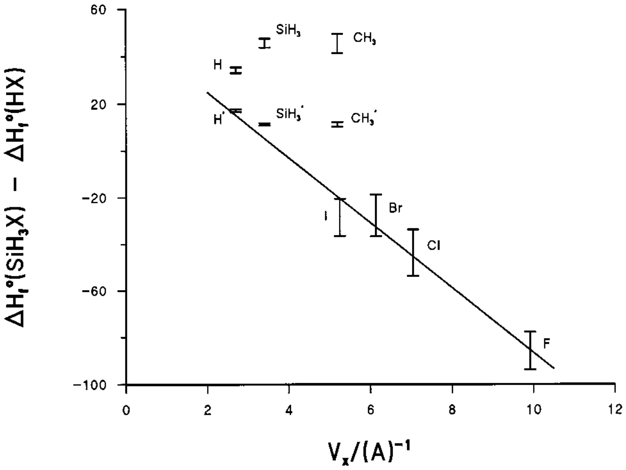

Figure 1. Correlation of Δ_1/kJ mol^{-1} with covalent potential. The primed points show the values for Δ_1/p (see text). The line shown is the best fit for F, Cl, Br, I, and H′.

TABLE 2: Enthalpy of Formation Data (kJ mol^{-1}) for the Trimethylsilyl/Methyl Compound Difference (Δ_2) Correlation with Electronegativity

X	V_x/(Å)$^{-1}$	$\Delta H_f°$(Me$_3$SiX)[a]	$\Delta H_f°$(MeX)[b]	Δ_2
OH	8.11	−500 ± 3	−201.7 ± 0.4	−298.3 ± 3
Cl	7.04	−354 ± 3	−82.0 ± 0.4	−272.0 ± 3
Br	6.13	−298 ± 4	−35.6 ± 1.2	−262.4 ± 4
I	5.25	−222 ± 4	+14.6 ± 1.3	−236.6 ± 4
CH$_3$	5.19	−233.2 ± 3	−83.7 ± 0.4	−149.5 ± 3
SiH$_3$	3.41	−111.8 ± 4	−29.1 ± 4[a]	−82.7 ± 6
H	2.70	−163.4 ± 4	−74.5 ± 0.4	−88.9 ± 4

[a] Data taken from ref 1. [b] Data taken from ref 4, except where stated.

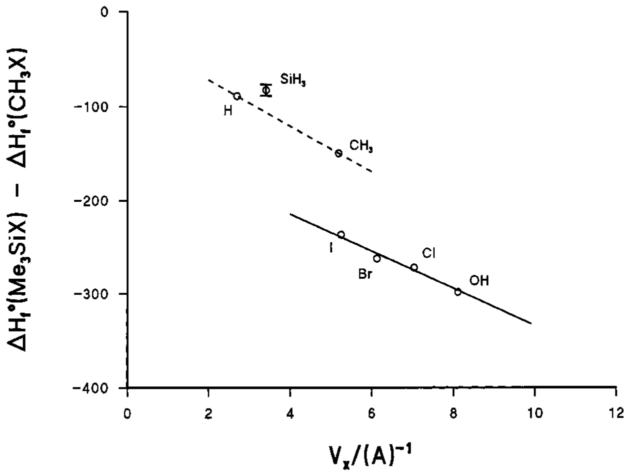

Figure 2. Correlation of Δ_2/kJ mol^{-1} with covalent potential. The solid line is the best fit for OH, Cl, Br, and I. The dashed line is the fit to the H and CH$_3$ only.

TABLE 3: Enthalpy of Formation Differences (Δ_3, kJ Mol^{-1})[a] between Trimethylsilyl and Silyl Compounds for the Correlation with Electronegativity

X	V_x/(Å)$^{-1}$	Δ_3
F	9.915	−209 ± 10
Cl	7.04	−218 ± 10
Br	6.13	−234 ± 10
I	5.25	−220 ± 9
CH$_3$	5.19	−204 ± 5
SiH$_3$	3.41	−192.1 ± 4
H	2.70	−197.7 ± 4

[a] See Tables 1 and 2 for specific $\Delta H_f°$ values, apart from $\Delta H_f°$(Me$_3$SiF) = −568 ± 6 kJ mol^{-1} from ref 1.

whereas the unmodified Δ_1(X = SiH$_3$) does not fit the correlation line, the modified value is quite close. If the small deviation is taken as significant, then to fit perfectly requires the suggested alteration[10] to $\Delta H_f°$(Si$_2$H$_6$). However for X = CH$_3$, neither Δ_1 nor Δ_1/p fit the correlation. The departure from the plot is significant and well beyond any experimental error. Our conclusion is that this correlation must be treated with caution. There may be deep-seated factors that cause such correlations to break down over too wide a range of compounds and that the use of the parameter p to improve things is questionable. This is discussed further below.

(ii) $\Delta_2 = [\Delta H_f°(\mathrm{Me_3SiX}) - \Delta H_f°(\mathrm{MeX})]$. The published enthalpy data for this correlation are shown in Table 2. These are essentially those used by LB[9], but once again we have added data for X = SiH$_3$ not previously included. Additionally the data sets for $\Delta H_f°$(Me$_3$SiBr) and $\Delta H_f°$(Me$_3$SiI) have been revised[1] as a result of new measurements.[1,12] Figure 2 shows the correlation between Δ_2 and V_x. LB[9] made substantial use of this plot. The good correlation line for X = OH, Cl, Br, and I was used to obtain estimates for $\Delta H_f°$(Me$_3$SiX) for X = F, NH$_2$, and SH. On the same basis we obtain slightly revised values of $\Delta H_f°$(Me$_3$SiF) = −568 kJ mol^{-1}, $\Delta H_f°$(Me$_3$SiNH$_2$) = −291 kJ mol^{-1}, and $\Delta H_f°$(Me$_3$SiSH) = −273 kJ mol^{-1}, compared to their values[9] of −572, −289, and −269 kJ mol^{-1}, respectively. LB[9] then argued that for molecules containing Si−X, where X possesses a lone pair, p → d π-type back-bonding occurs between X and Si, strengthening the bond in a similar way for all such molecules. The idea was reinforced by drawing a line through the two points X = H, CH$_3$ that is nearly parallel to the first line. Since π-type back-bonding is not possible for X = H, CH$_3$, this seemed a persuasive argument in favor of a constant p → d back-bonding contribution for those cases where it is possible. However, the inclusion of the X = SiH$_3$ points complicates the issue since it does not lie on the X = H, CH$_3$ line although there is no question of π-type bonding in Si−Si bonds. Either this correlation does not work for X = H, SiH$_3$, and CH$_3$, or a revision of ca. −23 kJ mol^{-1} is necessary for $\Delta H_f°$(Me$_3$SiSiH$_3$) (taking it from −112 to −135 kJ mol^{-1}). It is true that $\Delta H_f°$(Me$_3$SiSiH$_3$) is not an experimentally determined quantity; its value has been obtained via interpolation[12] between $\Delta H_f°$(Si$_2$H$_6$) and $\Delta H_f°$(Me$_3$SiSiMe$_3$). Such interpolations, however have strong backing evidence[1,13] and have been used by LB themselves.[3,10] That $\Delta H_f°$(Me$_3$SiSiH$_3$) should be in error by such an amount seems extremely unlikely. It is worth noting that the change required for $\Delta H_f°$(Me$_3$SiSiH$_3$) to make it fit the Δ_2 correlation with V_x would not be consistent with the change required to make $\Delta H_f°$(Si$_2$H$_6$) fit the correlation of Δ_1/p with V_x.

(iii) $\Delta_3 = [\Delta H_f°(\mathrm{Me_3SiX}) - \Delta H_f°(\mathrm{SiH_3X})]$. The published enthalpy data for this correlation are shown in Table 3. They are essentially those used by LB,[9] but with the small modifications to $\Delta H_f°$(Me$_3$SiBr) and $\Delta H_f°$(Me$_3$SiI) mentioned earlier. The plot is drawn in Figure 3 , and the line shown can only be tolerably well-defined provided one uses $\Delta H_f°$(Me$_3$SiF) obtained from the Δ_2 versus V_x correlation. This then suggests the probable deviation of the X = I point and is consistent with the revision of $\Delta H_f°$(SiH$_3$I) as recommended[9] and as indicated by the Δ_1 versus V_x correlation. Once again the Δ_3 values for molecules with the nonhalogenated substituents do not fall on the line, even within fairly large experimental errors. This implies that the methyl substituent effect on the Si−X bond dissociation energies cannot correlate smoothly with electronegativity across this range of substituents, X. Thus again this correlation, while having some value, is also limited in its scope.

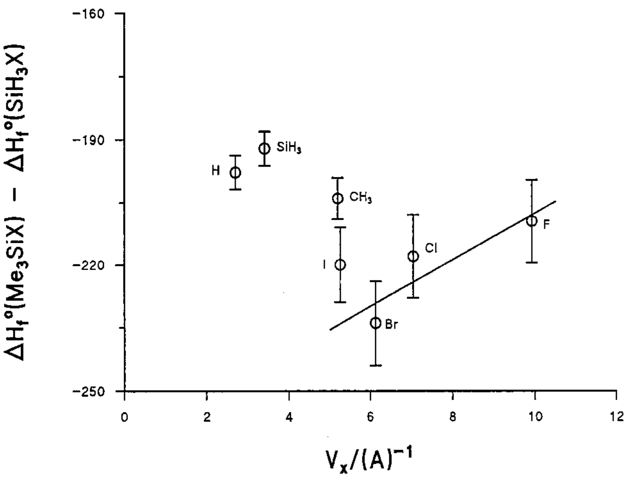

Figure 3. Correlation of Δ_3/kJ mol^{-1} with covalent potential. The solid line is the best fit for F, Cl, and Br.

TABLE 4: Standard Enthalpies of Formation (kJ mol^{-1}) of Silanes

compound	$\Delta H_f°$ [a]
SiH_4	34.3 ± 1.2
Si_2H_6	80.0 ± 1.5
Si_3H_8	121 ± 4.4

[a] Data taken from ref 1.

(iv) $\Delta_{4,m} = [\Delta H_f°(Me_mSi_{3-m}X) - \Delta H_f°(CH_3X)]$. This is a series of three correlations depending on whether $m = 1$, 2, or 3, which have been discussed by LB.[10] When $m = 3$ this becomes the correlation Δ_2 versus V_x discussed by us above. Unfortunately for $m = 1$ or 2 they become a series of "two-point lines", since the data are only available for X = H, CH_3. We do not show these in a figure here but LB[10] have derived the relationship:

$$\Delta_{4,m}/\text{kcal mol}^{-1} = (41.1 - 15.5m) - (5.23 + 0.20m)V_x \quad (1)$$

They then assume that this applies to *all* substituents *not* participating in p → d π-type back-bonding (another similar, but not identical, equation is derived for the π-type back-bonding substituents, viz, halogen, OH, SH, and NH_2). From this equation a set of group additivity values[14] was derived among which was $\Delta H_f°[Si-(Si)(H)_3] = 32.6$ kJ mol^{-1}, consistent with $\Delta H_f°(Si_2H_6) = 65$ kJ mol^{-1}. This is very closely equivalent to taking the equation above with $m = 0$ and $V_x = 3.41$ (Si), which gives $\Delta H_f°(Si_2H_6) = 68$ kJ mol^{-1}. This is the origin of the claim by LB[10] that the experimental value of 80 kJ mol^{-1} might be in error and need revision. From the considerations in this paper we see that the claim originates from the assumption that data for SiH_3 substituents should lie on the two-point correlation lines for H and CH_3 substituents, a questionable argument at best.

The Reliability of $\Delta H_f°(Si_2H_6)$. We briefly review the experimental evidence for this quantity here. The original data was obtained by Gunn and Green[15] using a calorimeter to measure the enthalpy of its explosive decomposition. With a subsequent but small change, due to a revision of the reference enthalpy of formation of amorphous silicon,[16] this led to $\Delta H_f°(Si_2H_6) = 80.0 \pm 1.5$ kJ mol^{-1}. Is there any reason to question this value? The enthalpies of formation of SiH_4, Si_2H_6, and Si_3H_8 (shown in Table 4) form a consistent set and are reasonably matched by theoretical calculations.[1] Thus if $\Delta H_f°(Si_2H_6)$ were in error almost certainly $\Delta H_f°(Si_3H_8)$ would have to be also (it was obtained by Gunn and Green[17] using the same method).

TABLE 5: Enthalpy of Formation Data (kJ mol^{-1}) for the Methyl/Hydrogen Compound Difference (Δ_5) Correlation with Electronegativity

X	V_x/(Å)$^{-1}$	$\Delta H_f°(CH_3X)$[a]	$\Delta H_f°(HX)$[b]	Δ_5	p[c]
F	9.915	−233.9 ± 2	−273.2 ± 0.8	+39.3 ± 2.2	1
OH	8.11	−201.7 ± 0.4	−241.8 ± 0.04	+40.1 ± 0.4	2
Cl	7.04	−82.0 ± 0.4	−92.3 ± 0.1	+10.3 ± 0.4	1
NH_2	6.67	−23.0 ± 0.4	−46.0 ± 0.4	+23.0 ± 0.6	3
Br	6.13	−35.6 ± 1.2	−36.3 ± 0.17	+0.7 ± 1.3	1
SH	5.77	−23.0 ± 0.8	−20.5 ± 0.4	−2.5 ± 0.9	2
I	5.25	+14.6 ± 1.3	+26.5 ± 0.13	−11.9 ± 1.3	1
CH_3	5.19	−83.7 ± 0.4	−74.5 ± 0.4	−9.2 ± 0.6	4
SiH_3	3.41	−29.1 ± 4.0	+34.3 ± 1.2	−63.4 ± 4.2	4
H	2.70	−74.5 ± 0.4	0	−74.5 ± 0.4	2
GeH_3	3.24	+42.2 ± 4[d]	+90.4 ± 2[e]	−48.2 ± 6	4
SnH_3	2.83	+117.6 ± 4[d]	+162.8 ± 2[e]	−45.2 ± 6	4

[a] Data taken from ref 4, unless otherwise stated. See also Table 2. [b] Data taken from ref 5, unless otherwise stated. See also Table 1. [c] See text for definition. [d] See text and ref 21. [e] From ref 15.

Another link in the sequence of $\Delta H_f°$ values of the silicon hydrides is $\Delta H_f°(SiH_2)$ with an impressively large number of recently consistent determinations,[1] in particular from the kinetics of the series of reactions

$$SiH_4 \rightleftarrows SiH_2 + H_2 \quad (2)$$

$$Si_2H_6 \rightleftarrows SiH_2 + SiH_4 \quad (3)$$

$$Si_3H_8 \rightleftarrows SiH_2 + Si_2H_6 \quad (4)$$

which have been studied in both directions under similar conditions, a consistent value of $\Delta H_f°(SiH_2) = 273 \pm 2$ kJ mol^{-1} emerges.[1,18,19] Thus the difference for $\Delta H_f°(Si_2H_6) - \Delta H_f°(SiH_4)$ can be linked to that of $\Delta H_f°(SiH_4) - \Delta H_f°(H_2)$. But since $\Delta H_f°(H_2)$ is zero, this links $\Delta H_f°(Si_2H_6)$ to $\Delta H_f°(SiH_4)$ directly. The equilibrium data give no indication of error in the value of 80 kJ mol^{-1} used for $\Delta H_f°(Si_2H_6)$ in any of these thermodynamic calculations. An error of 16 kJ mol^{-1} (as required by LB[10]) would give serious inconsistencies.

Further Correlations

These considerations lead us finally to try to assess the original correlation[5] from which all these arguments over silicon and organosilicon thermochemistry have arisen. This was the correlation of $\Delta_5 = [\Delta H_f°(MeX) - \Delta H_f°(HX)]$ versus V_x. The data for this correlation are shown in Table 5. They are essentially those used by LB[5] but with figures for X = GeH_3 and SnH_3 added. Figure 4 shows the correlation between Δ_5 and V_x. It is immediately apparent that the unmodified data show a good deal of scatter around any attempted correlation line. This led LB[5] to introduce the parameter p (vide supra) and modify the correlation to Δ_5/p versus V_x. This then neatly splits the data into two groups, the diatomic HX molecules and the polyatomic HX species, which then correlate around two separate but distinct straight lines of different slope (as shown). Once again this is beguilingly appealing but can lead to deception. We have added the points for X = GeH_3 and SnH_3 (for which $p = 4$), and it can be seen that these added $\Delta_5/4$ values do not fit very well the polyatomics correlation line. To obtain the data for these points, we have had to consider some estimated thermochemistry. This involves $\Delta H_f°(MeGeH_3) = 42 \pm 4$ kJ mol^{-1} and $\Delta H_f°(MeSnH_3) = 118 \pm 4$ kJ mol^{-1}. These are obtained by linear interpolation between the values for $\Delta H_f°(MH_4)$ and $\Delta H_f°(MMe_4)$ for M = Ge and Sn. The procedure is known to work well for M = Si.[20] The enthalpy

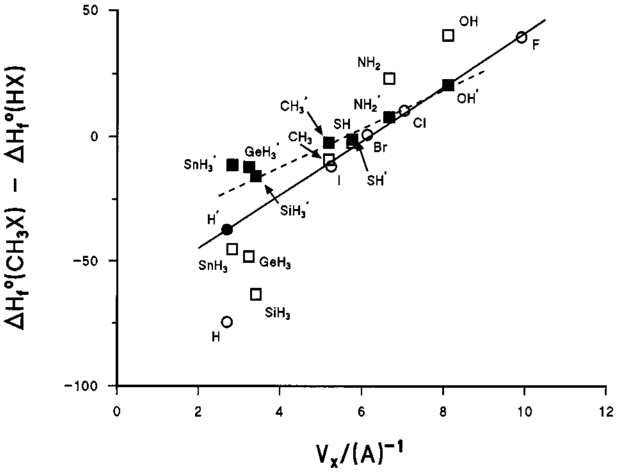

Figure 4. Correlation of Δ_5/kJ mol^{-1} (points represented by open symbols: atoms, circles; polyatoms, squares) with covalent potential. The primed points (solid symbols) show the values for Δ_5/p (see text). The solid line is the best fit for F, Cl, Br, I, and H′. The dashed line is the best fit for OH′, NH$_2$′, SH′, CH$_3$′, and SiH$_3$′.

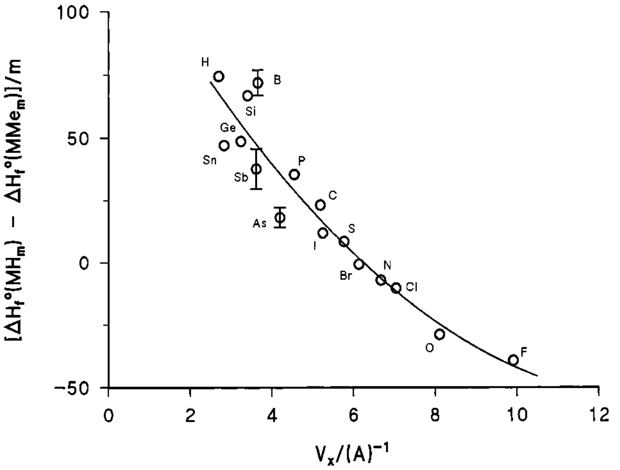

Figure 5. Correlation of Δ_6/kJ mol^{-1} with covalent potential. The curve represents a best fit to all the data.

TABLE 6: Average Enthalpy Differences (Δ_6, kJ Mol^{-1})[a] on Hydrogen-for-Methyl Substitution for the Correlation with Electronegativity

X	V_x/(Å)$^{-1}$	$\Delta H_f°$(Me$_m$X)	$\Delta H_f°$(H$_m$X)	m	Δ_6
B	3.66	−123 ± 10[b]	+92 ± 10[c]	3	+72 ± 5
C	5.19	−167.4 ± 0.7[b]	−74.5 ± 0.4	4	+23.2 ± 0.2
Si	3.41	−233.2 ± 3	+34.3 ± 1.2	4	+66.9 ± 0.8
Ge	3.24	−103.8 ± 8[d]	+90.4 ± 2[e]	4	+48.6 ± 2.1
Sn	2.83	−20.3 ± 1.9[d]	+162.8 ± 2[e]	4	+45.8 ± 0.7
N	6.67	−23.7 ± 0.6	−46.0 ± 0.4	3	−7.4 ± 0.2
P	4.55	−101.1 ± 5.3[b]	+5.4 ± 1.7[e]	3	+35.5 ± 1.9
As	4.20	+12.6 ± 10.1[b]	+66.5 ± 2[f]	3	+18.0 ± 3.4
Sb	3.62	+32.1 ± 25.2[b]	+145.1 ± 0.4[f]	3	+37.7 ± 8.4
O	8.11	−184.0 ± 0.5[b]	−241.8 ± 0.04	2	−28.9 ± 0.3
S	5.77	−37.5 ± 0.5[b]	−20.5 ± 0.4[g]	2	+8.5 ± 0.5
F	9.915	−233.9 ± 2	−273.2 ± 0.8	1	−39.3 ± 2.2
Cl	7.04	−82.0 ± 0.4	−92.3 ± 0.1	1	−10.3 ± 0.4
Br	6.13	−35.6 ± 1.2	−36.3 ± 0.17	1	−0.7 ± 1.3
I	5.25	+14.6 ± 1.3	+26.5 ± 0.13	1	+11.9 ± 1.3
H	2.70	−74.5 ± 0.4	0	1	+74.5 ± 0.4

[a] Data taken from previous tables unless stated. [b] From ref 23. [c] From ref 24. [d] From ref 21. [e] From ref 15. [f] From ref 25. [g] From ref 5.

values for MH$_4$ and MMe$_4$ have been taken from a recent review of organogermanium and organotin thermochemistry[21] and are thought to be reliable. LB[5] did not consider these arguments but in fact confidently suggested that the polyatomic correlation of Δ_5/p versus V_x was good enough to predict $\Delta H_f°$(MeGeH$_3$) = 18 ± 8 kJ mol^{-1} and $\Delta H_f°$(MeSnH$_3$) = 78 ± 8 kJ mol^{-1}, values well outside the limits of our estimates (and currently accepted experimental error). Thus here again the problem with this correlation is that it only works with a limited set of data and with the dubious use of the parameter p.

Interestingly, Benson, Francis, and Tsotsis[22] had earlier published the nearly equivalent correlation of average Me-for-H replacement enthalpy versus Pauling electronegativity and found the best correlation showed significant curvature. The advantage of this earlier correlation was that by using average Me-for-H replacement energies, the correlation could draw on a significantly larger database than LB.[5] The disadvantage is that only *average* Me-for-H replacement enthalpy values are used and for some specific sets of molecules (e.g., H$_2$O, MeOH, Me$_2$O) particular Me-for-H replacement enthalpies vary significantly from one another and therefore the average. It would appear that this is a particular problem with first row elements but may not be serious for elements in other rows of the periodic table. To compare directly the approach of Benson, Francis, and Tsotsis[22] that of with LB,[5] we have redrawn the former correlation of $\Delta_6 = (1/m)[\Delta H_f°(\mathrm{H}_m\mathrm{X}) - \Delta H_f°(\mathrm{Me}_m\mathrm{X})]$ with V_x instead of χ_m (Pauling electronegativity). This is shown in Figure 5 , and the data are listed in Table 6. Curvature in the new correlation is confirmed, as well as a certain amount of scatter, *i.e.*, just as with the old correlation.[22] Division of the Δ_6 values by p (which is equal to m) shrinks the spread of values somewhat but does not lead, in our view, to a better correlation; *i.e.*, there is still scatter beyond experimental error. Whether or not new experimental data will improve the correlation remains for future studies, but where data is of reasonable quality it seems that perfect correlation is elusive, and in particular linear correlation.

Conclusions

In summary we conclude that enthalpy difference correlations with electronegativity do have some value, provided sufficient data is available and conclusions are not overdrawn. The use of the "covalent potential" as proposed by Luo and Benson[3−11] as the best modern scale of electronegativity is not contradicted by these findings. The danger of two-point correlations is shown in the erroneous predictions for $\Delta H_f°$(Si$_2$H$_6$). The danger of the parameter, p, is shown by erroneous predictions for $\Delta H_f°$(MeGeH$_3$) and $\Delta H_f°$(MeSnH$_3$).

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