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The energetics of fluorinated species: estimation, enthalpies of formation, and electronegativity[1]

Deborah L. Kunkel[2], Andrew D. Fant[3], Joel F. Liebman*

Department of Chemistry and Biochemistry, University of Maryland, Baltimore County Campus, Baltimore, MD 21228-5398, USA

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Abstract

The literature estimation approach of assuming a near zero difference of the enthalpies of formation of condensed phase fluoro and hydroxy compounds (YF and YOH) is discussed. Reasoning based on phase change enthalpies, substituent effects, and our AMl calculations reported here, show that the difference depends strongly on the electronegativity of the element Y with comparatively little effect on its local environment. The assumption of a near constant difference of enthalpies of formation of organic fluorine compounds and their oxygen analogs is legitimized. Related, but admittedly more preliminary, regularities for the enthalpies of fluorinated species are also presented.

Introduction

The study of the energetics of species containing fluorine contains numerous surprises, as enunciated in the research reviews cited in the references [1]. The combination of small size, small polarizability, and high electronegativity of fluorine results in often contradictory results and derived conclusions. For example, it is unequivocal that the ionization potential of atomic fluorine is higher than any other element save helium and neon, yet the ionization potential corresponding to the energy needed for the removal of a π electron from a planar, and either partially or perfluorinated, species is accompanied by but a small change from the parent, unfluorinated species. By contrast, the ionization potential corresponding to removing a σ electron from the fluorine containing species is much higher than that of the parent compound. Atomic fluorine emphatically wants another electron to form the closed shell F^- anion and has an electron affinity higher than all but one other element. Yet once fluorine is chemically bound and has its completed octet, it fills the formally vacant 2p orbital on carbon in CF_2 via π overlap and formal electron donation so successfully that the former species is a quite stable, closed shell compound, despite its divalent carbon. Relatedly, fluorine directly attached to the cationic center of numerous carbonium ions results in stabilization, while should the fluorine be further away and thus not directly attached, a destabilized ion results.

Intermolecular forces between the hydrogen and fluorine atoms of different molecules of HF are strong, and so hydrogen fluoride is "almost" a

* Corresponding author.

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[2] Present address: Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA.

[3] Present address: Frederick Biomedical Supercomputing Center, NCI Frederick Cancer Research and Development Center, P.O. Box B, Frederick, MD 21706-1201 USA.

liquid under ambient conditions. Diatomic fluorine and hydrogen, lacking either hydrogen or fluorine respectively, have much lower boiling points with that of F_2 considerably higher than H_2 as befits its greater number of electrons and molecular weight. By contrast, a parent hydrocarbon and its perfluorinated derivative typically have comparable enthalpies of vaporization to each other, and to those of their partially fluorinated analogs. Indeed, for substituted organic compounds, replacement of hydrogen by fluorine in "non-crucial sites" (e.g. the hydrogen atom in the O–H bond of alcohols and acids) has relatedly little effect on the enthalpy of vaporization — if a trend were to be enunciated, one would conclude that fluorination results in increased ease of vaporization.

Neither experiment nor theory is particularly kind to the investigator of the chemical energetics of fluorinated species. It is considerably harder to burn highly or perfluorinated organic compounds in oxygen than their parent species and so oxygen bomb calorimetry has proven difficult and often unreliable for fluorocarbons [2]. Both F_2 and HF are notably corrosive but have been tamed by skillful experimentalists [3]. Yet the ill-defined but unquestionably oligomeric behavior of the latter (another manifestation of strong intermolecular H–F bonds) has precluded to date fluorine bomb calorimetry [4] from filling the slack so that one can obtain enthalpies of formation of fluorinated species that contain hydrogen as well [5]. In addition, in a well-acknowledged failure of molecular orbital theory and calculational quantum chemistry [6], F_2 has long been known to be unbound at the Hartree–Fock limit relative to the separated atoms. The F–F bond is among the weakest of single bonds, but it is not as weak as this would imply! Given the above complications and complexities, it is thus not surprising that the fluorine chemistry community has encouraged the development of convenient, albeit approximate, rules and regularities. The above cited ones on ionization potentials, enthalpies of vaporization, and carbene and carbonium ion stability, are but samples of the reasoning employed and patterns espoused in this discipline.

Is there a constant difference of the enthalpies of formation of Y–F and Y–OH species?

Among the other convenient energetics pattern for fluorinated compounds is the suggested "closeness" of the enthalpies of formation of corresponding condensed phase species with Y–F and Y–OH bonds, i.e.

$$\Delta H_f(\text{cond., YF}) \approx \Delta H_f(\text{cond., YOH}) \quad (1)$$

This rule [7] originated in Benson's review of the thermochemistry of sulfur containing species in which he made use of the comparative energetics of fluorosulfate and bisulfate salts, e.g. $\Delta H_f(\text{s, } Na^+FSO_3^-) = -1122.1\,\text{kJ mol}^{-1}$ and $\Delta H_f[\text{s, } Na^+(HOSO_3^-)] = -1125.5\,\text{kJ mol}^{-1}$, for which there is the derived enthalpy of formation difference, $\delta\Delta H_f(\text{s, "}NaSO_3\text{"}) \equiv [\Delta H_f(\text{s, } Na^+FSO_3^-) - \Delta H_f(\text{s, } Na^+HOSO_3^-)]$, which is numerically equal to $-1122.1 - (-1125.5) = 3.4\,\text{kJ mol}^{-1}$. (These enthalpies of formation, like nearly all other experimentally measured enthalpies of formation and energetics information used in the current study, were taken from Ref. 8.) Benson's assertion of near equality for sulfur–fluorine and sulfur–hydroxy compounds has been extended to the energetics of a variety of general organic and inorganic fluorine and oxygen containing species, much by Woolf [9] and some by an author of this paper [1(d)]. Application has been made to both the condensed phase and gaseous phase, and a "constant correction" for the hydrogen bonds (found only in condensed phase YOH species) was suggested and rationalized in terms of their "generic" strength of approximately $25\,\text{kJ mol}^{-1}$. For example, $\Delta H_f(\text{lq, } C_6H_5OH) = -153.6\,\text{kJ mol}^{-1}$ and $\Delta H_f(\text{lq, } C_6H_5F) = -150.6\,\text{kJ mol}^{-1}$; and $\Delta H_f(\text{g, } C_6H_5OH) = -96.4\,\text{kJ mol}^{-1}$ and $\Delta H_f(\text{g, } C_6H_5F) = -116.4\,\text{kJ mol}^{-1}$. (Note, the enthalpy of formation value for liquid was obtained by summing the enthalpy of formation of the solid phenol from Ref. 8c and the

enthalpy of fusion from Ref. 10; perusal of the references cited shows that it is not uncommon in this fluoro vs. hydroxy comparison to "mix" phases, and so liquid fluorobenzene would thus be compared with solid phenol, with its accompanying ΔH_f of $-165.1\,kJ\,mol^{-1}$.)

Concomitantly, the suggested near equality of enthalpies of formation of YF and YOH species has been extended to that of *gem*-difluoro species $Y(-F)_2$ and oxo species YO (with an explicitly included equivalent of water) because of the general absence of data on the corresponding dihydroxy species $Y(OH)_2$ — we recall the simple fact that most of these gem-diols have not been isolated because they readily decompose to $YO + H_2O$. Where Y is some organic group, i.e. the fluorine and oxygen atoms bonding to some carbon atom in the molecule, this appended regularity has proven quite accurate and therefore successful and useful. For example, acknowledging that we are "mixing" liquid and solid phase data, we find from our thermochemical archives that the enthalpies of formation of $C_6H_5CF_3(lq)$ and of $[C_6H_5COOH(s) + H_2O(lq)$, in lieu of $C_6H_5C(OH)_3)$ (cond.)] are the numerically comparable -637.6 and $-627.0\,kJ\,mol^{-1}$, respectively.

Most of the examples presented above are for organic compounds. What about for general Y? Problems were earlier acknowledged for some pairs of similarly related fluorine and oxygen containing compounds, e.g. $\Delta H_f(g,\ F_2) = 0.0$ by definition while $\Delta H_f[g,\ H_2O_2 = (OH)_2)] = -136.31\,kJ\,mol^{-1}$ resulting in $\delta\Delta H_f(g,\ \text{"}(\_)_2\text{"}) \equiv 1/2[\Delta H_f(g,\ F_2) - H_f(g,\ H_2O_2)] = 1.2[0.0-(-136.3)] = 68.2\,kJ\,mol^{-1}$. Yet, despite this major numerical disparity, it has been hard to dismiss this exceptionally useful and conceptually simple regularity for the energetics of fluorinated species.

Electronegativity effects on the difference of the enthalpies of formation of Y–F and Y–OH species

In the current paper, we discuss the strengths, limitations and origin of this regularity using a composite of experimental and computationally derived enthalpies of formation. To begin with, it is at least a posteriori unavoidable that a constant difference of $\Delta H_f(g,\ YF)$ and $\Delta H_f(g,\ YOH)$ cannot be valid for any and all Y. After all, let Y be "monomeric nothing", i.e. let us compare the enthalpies of formation of gaseous fluorine and OH. The appropriate values are 78.99 and $38.95\,kJ\,mol^{-1}$ with a derived enthalpy of formation difference, $\delta\Delta H_f(g,\ \text{"\_"}) \equiv [\Delta H_f(g,\ F) - \Delta H_f(g,\ OH)] = 40.0\,kJ\,mol^{-1}$. What groups Y should be affixed? Using language which the organic chemist is more accustomed to, what are the most electron-donating and electron-withdrawing groups or "substituents"?

The former groups, the most electron-donating species, are naturally assumed to be the alkali metals, and then this answer is easily subsumed by the suggestion of a "free electron". That is, we consider and contrast F^- and OH^-. Although the electron affinity of fluorine is not the highest of all elements (that of chlorine is higher than that of fluorine by $21.0\,kJ\,mol^{-1}$), $EA(F)$ is nonetheless significantly higher than $EA(O)$ and $EA(OH)$ by 187.0 and $151.5\,kJ\,mol^{-1}$, respectively. As such, $\delta\Delta H_f(g\ \text{"}^-\text{"}) = [\Delta H_f(g,\ F^-) - \Delta H_f(g,\ OH^-)]$ should be significantly smaller, i.e. more negative, than the $40.0\,kJ\,mol^{-1}$ for the difference of the enthalpy of formation of the corresponding neutrals. And indeed it is: we find the enthalpy difference is $[-255.39 - (-143.5)] = -111.9\,kJ\,mol^{-1}$. Relatedly, the most electron-withdrawing group would totally remove the electron and so cations would take preeminence. Because the ionization potential of fluorine is significantly higher than that of oxygen or OH, $\delta\Delta H_f(g\ \text{"}^+\text{"}) \equiv [\Delta H_f(g,\ F^+) - \Delta H_f(g,\ OH^+)]$ is expected to be significantly larger, i.e. more positive, than the $40.0\,kJ\,mol^{-1}$ of the neutrals. This is likewise realized: the enthalpy difference is now $(1766.4 - 1289.5) = 476.9\,kJ\,mol^{-1}$.

Of course, we can be accused of being a bit disingenuous in that total electron donation of anything to fluorine is not achieved in any neutral species, even the fluorides of the alkali metals. No

Table 1
Experimentally measured enthalpies of formation of a set of gaseous YF and YOH, the difference between these quantities, and the electronegativity of the associated Y

Y	ΔH_f(g, YF) (kJ mol^{-1})	ΔH_f(g, YOH) (kJ mol^{-1})	$\delta\Delta H_f$(g, Y) (kJ mol^{-1})	x(Y)
Li	−339.8	−238.1	−101.7	1.0
H	−271.1	−241.8	−29.3	2.1
$CH_3(CH_2)_2$ [a]	−285.9	−255.1	−30.8	2.5
$(CH_3)_2CH$ [a]	−293.5	−272.8	−20.7	2.5
Cl	−54.5	−78.7	24.2	3.0
OH	−98	−136.3	38	3.5
F	0	−98	98	4.0

[a] These are, quite astonishingly, the sole two examples known to the authors for which there are classical calorimetric data on the enthalpy of formation of an alkyl fluoride, i.e. a saturated hydrocarbon chain attached to only a single fluorine atom.

anion, save F^- itself, contains unit negatively charged fluorine. Relatedly, no neutral or cationic species contains unit-plus charged fluorine (save F^+ itself), despite the synthetic utility of species formally containing electrophilic, and hence presumed positive, fluorine. It is more reasonable to consider partially and most generally negatively charged fluorine, for which the amount of charge transfer is related to the relative electronegativity of fluorine and what it is attached to. Experiment (see Table 1) shows that a rough trend prevails for some suitably simple fluorides and hydroxides, for which there is only one fluorine or OH affixed to the Y, and no stabilizing π interactions between the Y and the affixed fluorine or OH are expected.

Can we do better than qualitatively relate the relative electronegativities and enthalpies of formation? Enthalpies of formation relate to bond energies. We recall Pauling's classic and venerable electronegativity relation [11], which in the generic form is:

$$D(\text{Y–Z}) = 1/2[D(\text{Y–Y}) + D(\text{Z–Z})] + k[x(\text{Y}) - x(\text{Z})]^2 \quad (2)$$

where D is the dissociation (bond) energy, x is the electronegativity, and k is unit dependent. It is natural to ask whether Eqs. (1) and (2) are compatible for all Y, or whether the compatibility in fact depends on a rather precise value of the electronegativity for the element Y. Our comparisons of F^+ with OH^+ and F^- with OH^- suggest the latter. Because we are expressing energies in kJ mol^{-1}, k equals $23 \times 4.184 = 96.2$. In the current study we let Z = F and OH, and so we have two equations:

$$D(\text{Y–F}) = 1/2[D(\text{Y–Y}) + D(\text{F–F})] + 96.2[x(\text{Y}) - x(\text{F})]^2 \quad (3a)$$

$$D(\text{Y–OH}) = 1/2[D(\text{Y–Y}) + D(\text{HO–OH})] + 96.2[x(\text{Y}) - x(\text{OH})]^2 \quad (3b)$$

D(F–F) and D(HO–OH) are well-established quantities. If we equate dissociation energies and dissociation enthalpies, then for arbitrary single bonds:

$$D(\text{Y–Z}) = -\Delta H_f(\text{g, YZ}) + \Delta H_f(\text{g, Y}) + \Delta H_f(\text{g, Z}) \quad (4)$$

From a major archival source of thermochemical information, we find ΔH_f(g, F) = 79.0 kJ mol^{-1}, ΔH_f(g, OH) = 39.0 kJ mol^{-1} and ΔH_f(g, HOOH) = −136.3 kJ mol^{-1} (and of course, by definition, ΔH_f(g, F_2) = 0). We thus derive D(F–F) = 158.0 and D(HO–OH) = 214.3 kJ mol^{-1}. Admitting that electronegativity-derived bond energy reasoning has never been intended to be accurate to a fraction of a kilojoule, we combine

Eqs. (3a), (3b) and (4) to give the numerically "relaxed" equations:

$$D(\text{Y–F}) = -\Delta H_f(\text{g, YF}) + \Delta H_f(\text{g, Y}) + 79 \quad (5a)$$

$$D(\text{Y–OH}) = -\Delta H_f(\text{g, YOH}) + \Delta H_f(\text{g, Y}) + 39 \quad (5b)$$

From Pauling we take $x(\text{F}) = 4.0$ and $x(\text{O}) = 3.5$. For conceptual simplicity, we let $x(\text{OH}) = x(\text{O})$. Equations (3a) and (3b) now become:

$$D(\text{Y–F}) = 1/2\{[D(\text{Y–Y})] + 158\} + 96[x(\text{Y}) - 4]^2 \quad (6a)$$

$$D(\text{Y–OH}) = 1/2\{[D(\text{Y–Y})] + 214\} + 96[x(\text{Y}) - 3.5]^2 \quad (6b)$$

Noting that the right-hand sides of Eqs. (5a) and (6a) are equal to each other, and likewise those of Eqs. (5b) and (6b), results in:

$$-\Delta H_f(\text{g, YF}) + \Delta H_f(\text{g, Y}) + 79 = 1/2\{[D(\text{Y–Y})] + 158\} + 96[x(\text{Y}) - 4]^2 \quad (7a)$$

$$-\Delta H_f(\text{g, YOH}) + \Delta H_f(\text{g, Y}) + 39 = 1/2\{[D(\text{Y–Y})] + 214\} + 96[x(\text{Y}) - 3.5]^2 \quad (7b)$$

Combining Eqs. (7a) and (7b) and then doing some simple algebra results in the general equation:

$$\Delta H_f(\text{g, HF}) - \Delta H_f(\text{g, YOH}) = 96x(\text{Y}) - 292 \quad (8)$$

References 1d and 9 document that there are data of sufficient quality and quantity to conclude that Eq. (1) is valid for organic fluoro and hydroxy species. It is well established that estimations of the enthalpies of vaporization of organic compounds are considerably more reliable than those of sublimation [12]. For example, we recall that there is a nearly constant increment for hydroxy species relative to the enthalpy of vaporization for their corresponding parent hydrocarbons [13], i.e.

$$\Delta H_v(\text{YOH}) \approx \Delta H_v(\text{YH}) + 30 \quad (9)$$

Recall, as noted earlier in the text, that

$$\Delta H_v(\text{YH}) \approx \Delta H_v(\text{YF}) \quad (10)$$

From Eqs. (1), (9) and (10) we conclude (for organic species at least) that

$$\Delta H_f(\text{g, YOH}) = \Delta H_f(\text{g, YF}) + 30 \quad (11)$$

Equations (8) and (11) are consistent when $x(\text{Y}) = 2.7$, comfortably close to the value of 2.5 generally cited as the Pauling electronegativity of carbon. In that the Pauling electronegativity of sulfur is also 2.5, we should not be surprised that Eq. (1) also works for sulfur containing fluorine and hydroxy compounds.

It is to be emphasized that the earlier vestiges of the element Y have disappeared apart from its electronegativity — neither its single bond energy Y–Y nor its enthalpy of formation as an atom, ΔH_f(g, Y), or as a "diatomic", ΔH_f(g, Y–Y), enter into the difference of the enthalpies of formation of YF and YOH, or of the dissociation energies of YOH and YF. We can thus quite cavalierly peruse the periodic table to check the validity of Eq. (8). For example, we note that all the alkali metals have electronegativities of 1.0 or somewhat less. Equation (8) predicts an enthalpy of formation difference of approximately $-200\,\text{kJ mol}^{-1}$, while for Li(v.s.), Na, K, and Cs the differences from experiment are −101.7, −84.1, −94.4 and $-112\,\text{kJ mol}^{-1}$. But we recall Pauling's caveats (in Ref. 11) as to the use of Eq. (2) for quantitatively understanding the energetics of compounds containing alkali metals.

AM1 computational results on the enthalpies of formation of Y–F and Y–OH species

Our intuition, as well as the somewhat more rigorous relation (Eq. (8)), still affirms that the fluorine containing species YF should gain thermodynamic stability relative to its hydroxy analog YOH as the electronegativity decreases. Yet, forgetting about examples from organic chemistry, justification from the experimental literature is sparse. Computational theory allows us to derive

Table 2
Normalized AM1 calculated difference in the enthalpies of formation (in kJ mol^{-1}) of a set of gaseous YF and YOH, and the Pauling electronegativity of the element Y

Element	$\delta\Delta^*(Y)$	$\delta\Delta^*2(Y)/2$	$\delta\Delta^3 3(Y)/3$	$\delta\Delta(Y)^*4/4$	$x(Y)$
B	−36.1	−33.9	−37.7		2.0
C	−16.7	−3.4	1.5	5.7	2.5
N	16.1	46.5	48.5		3.0
O	52.9	85.9			3.5
Al	−118.6	−118.2	−121.1		1.5
Si	−90.6	−92.3	−88.5	−89.1	1.8
P	−29.4	−15.9	−14.3		2.1
S	−38.1	−24.0			2.5

many of the missing enthalpies of formation for the desired comparisons. We can likewise also directly study the energetics of species with two (or more) geminal hydroxy groups without concern about the idiosyncracies of the relative strengths of the two Y–O σ bonds in $Y(OH)_2$ and the π bond in YO. Relatively, we can inquire how multiple substitution by fluorine and hydroxy impacts their relative enthalpies of formation. To do all of the above, and to bypass the various thermochemical corrections and connections between quantum chemical total energies and experimental enthalpies of formation, we opted to use the AM1 method [14] within the MOPAC 6.0 program package protocol [15]. Acknowledging that AM1 is a parametrized theory, we also avoided inclusion of those species for which there is only one example of the type of bond of interest. As such, all diatomic molecules (e.g. HF, ClF and F_2) were ignored. Table 2 presents the calculated "normalized" differences (i.e. per affixed group) for a collection of fluorides and hydroxides, where it is always assumed that Y has its normal covalence. For example, $\delta\Delta^*(C)$ is the difference in the enthalpies of formation of CH_3OH and CH_3F, $[\delta\Delta^*2(P)]/2$ is the difference for $PH(OH)_2$ and PHF_2, and $[\delta\Delta^*3(N)]/3$ is the difference for $N(OH)_3$ and NF_3.

Because we are primarily interested in trends, we defer to Appendix A the calculated normalized enthalpies of formation for the species from which the entries in Table 2 were derived. Numerous complications would arise if we wished to compare theory and experiment. For example, for the three pairs of fluoro and hydroxy compounds used to illustrate our "$\delta\Delta^*$" symbolism, we know of: (a) no direct calorimetric measurement of the enthalpy of formation of CH_3F despite its certain thermodynamic stability; (b) no experimental evidence for $PH(OH)_2$ — this species spontaneously rearranges to form the "normal" form of hypophosphorous acid, $H_2P(O)OH$, with its two P–H bonds and a strong phosphoryl (phosphine oxide) bond; and (c) no experimental evidence for the "ortho" acid $N(OH)_3$ — we can only assume that it spontaneously decomposes to form nitrous acid, which in turn is quite unstable and has a tendency to decompose further into NO, NO_2 and water.

It can be seen that the desired difference in the enthalpy of formation of YF and YOH is primarily dependent on the electronegativity of the central element Y with a secondary dependence on the number of affixed fluoro or hydroxy groups. This can be fine-tuned somewhat. Consider the differences for a given element Y (see Table 2) as one traverses multiple substitution and normalize it by the valence of the element, e.g. for carbon consider $\delta\Delta^*(C)$, $\delta\Delta^*2(C)/2$ $\delta\Delta^*3(C)/3$ and $\delta\Delta^*4(C)$. Although not universally, and certainly not linearly, it can be seen that the differences generally become more positive with increasing fluoro and hydroxy substitution. This finding is in accord with our electronegativity reasoning in that with

increasing substitution by either group, the electronegativity of the central Y atom is expected to increase and so $\delta\Delta^*$ is expected to become more positive. After all, cationic species generally seem to have a more positive value of fluorine vs. hydroxy enthalpy of formation difference than do their corresponding neutrals. For example, while the difference for fluorobenzene and phenol is $-20\,kJ\,mol^{-1}$, it is increased to 37 and $50\,kJ\,mol^{-1}$ for protonation and ionization, respectively. Relatedly, the difference of $-12\,kJ\,mol^{-1}$ separating acetyl fluoride and acetic acid is increased to 71 upon ionization, and while there are seemingly no thermochemical data for $CH_3C(F)OH^+$ corresponding to protonation of the former species, the normalized difference value for $CH_3CF_2^+$ and $CH_3C(OH)_2^+$ is $78\,kJ\,mol^{-1}$.

Consider the range of enthalpy differences for a given element Y (see Table 2) as one traverses multiple substitution and normalize it by the valence of the element, e.g. for carbon consider $1/4[\delta\Delta^*(C) - \delta\Delta^*(C)/4]$ and for B, $1/3[\delta\Delta^*(B) - \delta\Delta^*3(B)/3]$. This normalized enthalpy range also generally increases with increasing electronegativity, although an electronegativity-based explanation evades us.

Preliminary findings on related regularities and some not so preliminary conclusions

Should the reader complain that most of the desired hydroxy species remain experimentally uncharacterized, it will be recalled that we have affirmed that the enthalpy of formation difference for corresponding gaseous species containing single C–F and C–OH bonds is really quite constant. It would appear that the student of the energetics of organic fluorine compounds has a powerful tool for estimating enthalpies of formation. But what about the student of the fluorine and the hydroxy compounds of other elements? It is well established that the energetics of Y–OH and Y–OCH_3 compounds are interrelated. It might have been assumed that there is a constant difference because it is the oxygen, and not Y, that is attached to the hydrogen atom and to the CH_3 group in turn. However, Guthrie [16] has analysed solution studies and found that the energetics depend strongly on the nature of Y. More precisely, he has shown that the Gibbs free energy for the reaction

$$Y\text{–}OCH_3 + H_2O \rightarrow Y\text{–}OH + CH_3OH \qquad (12)$$

linearly relates to the acidity of the YOH via Eq. (13)

$$\Delta G = -20.0(\pm 1.2) + 1.41(\pm .10)pK_a(YOH) \qquad (13)$$

once correction has been made for steric and symmetry effects. (Not surprisingly, this equation is also limited to those acids in which resonance does not stabilize the anion relative to the neutral. For our collection of Y, we may thus expect that ΔH_f(g, $YOCH_3$) should generally interrelate with ΔH_f(g, YOH) and thus with ΔH_f(g, YF).) The enthalpy of formation differences of ΔH_f(g, YF) and ΔH_f(g, $YOCH_3$), designated by us as $\delta'\Delta^*(Y)$, are given in Table 3, from which it can be seen that these quantities predictably track the electronegativity of Y. This is fortunate in that numerous species of the type $Y(OCH_3)_n$ are known while the parent $Y(OH)_n$ are not. Preliminary findings show normalized differences of ΔH_f(g, YF_n) and ΔH_f(g, $Y(OCH_3)_n$) relate to

Table 3
AM1 calculated differenced of the enthalpies of formation (in $kJ\,mol^{-1}$) of a set of gaseous YF and YOH, and YF and $YOCH_3$ (designated $\delta\Delta^*(Y)$ and $\delta'\Delta^*(Y)$, respectively) and the Pauling electronegativity of the element Y

Element	$\delta\Delta^*(Y)$	$\delta'\Delta^*(Y)$	$x(Y)$
B	−36.1	−76.4	2.0
C	−16.7	−32.8	2.5
N	16.1	9.7	3.0
O	52.9	33.2	3.5
Al	−118.6	−130.5	1.5
Si	−90.6	−103.3	1.8
P	−29.4	−40.3	2.1
S	−38.1	−31.4	2.5

those of the $\Delta H_f(g, YF_n)$ and $\Delta H_f(g, Y(OH)_n)$. From the data in Table 2, we find the normalized differences of the fluoro and hydroxy species of Y = Al, Si and B have the narrow total ranges from −118.6 to −121.1, −88.5 to −92.3, and −33.9 to −37.7 kJ mol^{-1}, respectively. The data in Appendix B show that the normalized differences for the corresponding fluoro and methoxy species range from −129.6 to −134.3, −103.3 to −111.2, and −76.4 to −88.7 kJ mol^{-1}. We are encouraged by these findings.

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Appendix A

Table A1
Normalized AM1 calculated differences of the enthalpies of formation (in kJ mol^{-1}) of our set of gaseous $YH_{p-n}F_n$ and $YH_{p-n}(OH)_n$. The data are organized in increasing atomic number of Y and then, for each element, by increasing n

Y	p	n	$\Delta H_f(g, YH_{p-n}F_n)/n$	$\Delta H_f(g, YH_{p-n}(OH)_n)/n$
B	3	1	−343.2	−307.1
		2	−381.6	−347.7
		3	−379.6	−341.9
C	4	1	−255.3	−238.6
		2	−242.8	−239.5
		3	−240.6	−242.0
		4	−236.0	−241.7
N	3	1	−53.6	−69.7
		2	−50.0	−96.4
		3	−55.8	−104.3
O	2	1	−94.1	−147.4
		2	+22.0	−64.0
Al	3	1	−382.8	−264.2
		2	−402.5	−284.3
		3	−398.7	−277.5
Si	4	1	−358.9	−268.4
		2	−379.6	−287.3
		3	−391.8	−303.2
		4	−399.5	−310.5
P	3	1	−261.0	−231.6
		2	−298.9	−282.9
		3	−319.3	−305.0
S	2	1	−191.6	−167.5
		2	−213.5	−175.4

Appendix B

Table B1
Normalized AM1 calculated differences of the enthalpies of formation (in kJ mol^{-1}) of our set of gaseous $YH_{p-n}F_n$ and $YH_{p-n}(OCH_3)_n$ for Y = Al, Si and B

Y	p	n	$\Delta H_f(g, YH_{p-n}F_n)/n$	$\Delta H_f(g, YH_{p-n}(OCH_3)_n)/n$
Al	3	1	−382.8	−252.3
		2	−402.5	−268.2
		3	−398.7	−269.0
Si	4	1	−358.9	−255.7
		2	−379.6	−275.1
		3	−391.8	−283.0
		4	−399.5	−288.4
B	3	1	−343.2	−266.8
		2	−381.6	−293.0
		3	−379.6	−300.9