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Heats of Formation of Alkyl Fluorides

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Current data on $\Delta_f H°_{298}$ of alkyl fluorides are reexamined from the point of view of internal consistency and new values are recommended for all of them. In particular, fairly large discrepancies are suggested for current values of $\Delta_f H°_{298}$ of *t*-BuF, *n*-PrF, *i*-PrF, and EtF.

The heat of formation of methyl fluoride was recently discussed by Liebman, Simões, and Slayden.[1] The $\Delta_f H°_{298}$(MeF) of −56 kcal/mol in the JANAF tables[2] was questioned by ref 1. "What methods can we use to derive a value for the enthalpy of formation of this compound?" [1] Liebman et al. asked. They used our new scale of electronegativity based on (V_x), the covalent potential, and tried to correlate V_x with heats of formation of *n*-propyl and isopropyl fluoride. They found there was a large deviation for the correlation. While questioning the accuracy of $\Delta_f H°_{298}$(MeF), they neglected to examine the data on $\Delta_f H°$(*n*-PrF) and $\Delta_f H°$(*i*-PrF). If the data on $\Delta_f H°$(*n*-PrF) and $\Delta_f H°$(*i*-PrF) are unreliable, such correlation becomes untenable and their suggested values of $\Delta_f H°_{298}$(MeF) must be questioned as well.

First we will discuss $\Delta_f H°_{298}$(MeF). The reliability of $\Delta_f H°$(*n*-PrF) and $\Delta_f H°$(*i*-PrF) will be examined in Appendixes 1 and 2.

Our electronegativity scale has proved a simple and useful measure for correlating molecular energetics during the past 8 years. It works well for heats of formation,[3,4] homo- and heterolytic bond dissociation energies,[3,5] ionization potentials,[3,6] Lewis acid strengths,[3,7] divalent state stabilization energies (DSSE),[8] electrostatic potentials,[9] and the Hammett plots.[10] It has been shown by a number of examples that Pauling, Mulliken, Allred-Rochow, and other scales of electronegativity do not work as well for such parameters. An important theoretical support for our scale V_x comes from the absolute electronegativity theory of Parr and Pearson.[3,11,12]

For predicting heats of formation of RX (where X represents one of wide variety of univalent atoms or more complex substituents), we first need to choose a reference point. Using this point and our methods, we can estimate many heats of formation. Figure 1 is a "molecular tree." It represents a map of relationships between heats of formation of important organic species.[13] From the $\Delta_f H°$ value of highest accuracy among them, the $\Delta_f H°$(RX) values for other species can be easily estimated by using the relationships. On the basis of molecular tree, heats of formation of many organometallic compounds have been estimated.[13]

For X = Cl, Br, I, and H, it is very reasonable that CH_3X are chosen as the anchor points. For fluorides, values of $\Delta_f H°$ of vinyl−F, phenyl−F, Pr−F, and *i*-Pr−F are the only ones listed.[14] $\Delta_f H°$(MeF) value is not listed[14] and is still controversial. We will examine vinyl and phenyl species as the anchor point of the fluorides. It is our opinion that $\Delta_f H°$ of Pr−F and *i*-Pr−F may be in error. Our reasons will be discussed in appendixes I and II.

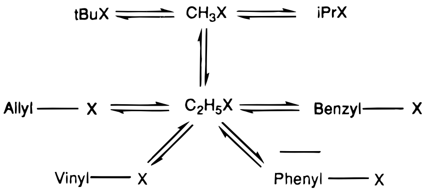

Figure 1. Thermochemical tree of relationships between heats of formation for some important organic species.

A simple empirical relationship between heats of formation for 37 pairs of vinyl and phenyl derivatives has been shown.[15]

$$\Delta_f H°(\text{vinyl}-X) - \Delta_f H°(\text{phenyl}-X) = -7.1(\pm 1.5)\ \text{kcal/mol} \quad (1)$$

For X = F, the difference was −5.5 ± 0.6 kcal suggesting that $\Delta_f H°$ data for C_2H_3F(−33.2 ± 0.4 kcal) and C_6H_5F(−27.7 ± 0.4 kcal) in ref 14 were self-consistent and possibly reliable.

The ΔH_f of the isodesmic reaction is

$$\text{vinyl}-H\ (\text{or phenyl}-H) + \text{ethyl}-X \rightarrow \text{vinyl}-X\ (\text{or phenyl}-X) + \text{ethyl}-H \quad (2)$$

has been used to describe a stabilization energy, E_c.[15,16]

$$\begin{aligned} E_c(\text{vinyl}-X) \equiv [\Delta H_2(\text{vinyl}-X)] &= \{\Delta_f H°(C_2H_3X) - \Delta_f H°(C_2H_5X)\} + [\Delta_f H°(C_2H_6) - \Delta_f H°(C_2H_4)] \\ &= \{\Delta_f H°(C_2H_3X) - \Delta_f H°(C_2H_5X)\} - 32.5 \pm 0.3\ \text{kcal/mol} \quad (3a) \end{aligned}$$

When E_2 (vinyl−X) is close to zero, the heats of hydrogenation of vinyl−X and ethylene are about the same. E_c is a measure of the differences in interaction of X with the π and σ bonds in ethane and ethylene referenced to H as a standard. A similar interpretation can be made in the case of phenyl.

$$\begin{aligned} E_c(\text{phenyl}-X) \equiv [\Delta H_r(\text{phenyl}-X)] &= \{\Delta_f H°(C_6H_5X) - \Delta_f H°(C_2H_5X)\} + \{\Delta_f H°(C_2H_6) - \Delta_f H°(C_6H_6)\} \\ &= \{\Delta_f H°(C_6H_5X) - \Delta_f H°(C_2H_5X)\} - 39.7 \pm 0.3\ \text{kcal/mol} \end{aligned}$$

Luo and Holmes found that E_c for both vinyl−X and phenyl−X are small and about 0 ± 1 kcal/mol[13] when X is a univalent atom (i.e., Cl, Br, I, and H). We thus may estimate for these species

$$\Delta_f H°(C_2H_5X)_{est} \approx -32.5 + \Delta_f H°(C_2H_3X)_{exp}\ \text{kcal/mol} \quad (4a)$$

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and

$$\Delta_f H°(C_2H_5X)_{est} \approx -39.7 + \Delta_f H°(C_6H_5X)_{exp}\ \text{kcal/mol} \quad (4b)$$

Assuming that F can be included in this series, we can deduce two independent values of $\Delta_f H°(Et-F)_{est}$ from eqs 4a and 4b, respectively,

$$\Delta_f H°(C_2H_5X)_{est} \approx -65.7\ \text{kcal/mol}$$

$$\Delta_f H°(C_2H_5X)_{est} \approx -67.4\ \text{kcal/mol}$$

An average value is -66.6 ± 1 kcal/mol.

A simple relation was found in our earliest work:[4a]

$$\Delta_f H°(RX) = \Delta_f H°(CH_3X) + [0.9 - 1.5m(m-1)] - \frac{m}{0.67 + 0.21m} V_x \quad (5)$$

Here m is equal to 1, 2, or 3 for primary, secondary, or tertiary carbon atoms. For EtF, $m = 1$ and with $V_x = 9.915$,[3] we rederive the heat of formation of methyl fluoride.

$$\begin{aligned}\Delta_f H°(CH_3F)_{est} &= \Delta_f H°(Et-F)_{est} - 0.9 + 11.3\ \text{kcal/mol} \quad (6)\\ &= \Delta_f H°(Et-F)_{est} + 10.4\ \text{kcal/mol}\end{aligned}$$

$$\Delta_f H°(CH_3F)_{est} \approx -55.3\ \text{kcal} \quad \text{if} \quad \Delta_f H°(C_2H_5X)_{est} \approx -65.7\ \text{kcal}$$

$$\Delta_f H°(CH_3F)_{est} \approx -57.0\ \text{kcal} \quad \text{if} \quad \Delta_f H°(C_2H_5X)_{est} \approx -67.4\ \text{kcal}$$

Both values are close to the value of $-53.9 \pm .8$ kcal/mol suggested in ref 1.

Below we introduce another method for predicting $\Delta_f H°(CH_3F)$. A good linear relationship between $[\Delta_f H°(CH_3X) - \Delta_f H°(HX)]/p$ and V_x was presented in our early work,[4d] where p is the number of hydrogen atoms in the HX molecule and $p = 1$ or 2 when X is a halogen or a hydrogen atom, respectively. For $\Delta_f H°(HX)$ of X = Cl, Br, I, and H, we have

$$\{\Delta_f H°(CH_3X) - \Delta_f H°(HX)\}/p = -16.14 \pm 2.63\ V_x \quad (7)$$

The correlation coefficient is 0.998 and the standard deviation is 0.4 kcal/mol. Using this correlation we have

$$\{\Delta_f H°(CH_3F)_{est} = \Delta_f H°(HX)_{exp} - 16.14 \pm 2.63 V_x = -55.4 \pm 1\ \text{kcal} \quad (8)$$

Our above-stated correlations based on eqs 6 and 7 are independent. They give $\Delta_f H°(CH_3F)_{est} = -55.3$, -57.0, and -55.4 ± 1 kcal/mol, respectively. The three values estimated are very close. The average value which we recommend is -55.9 ± 1 kcal/mol, very close to -56 ± 7 kcal/mol in the JANAF Tables.

$\Delta_f H°(MeF)$ was estimated by five methods,[1] and an average value was recommended of -53.9 ± 0.8 kcal. For four of the methods, data of $\Delta_f H°(n\text{-PrF})$ and $\Delta_f H°(i\text{-PrF})$ were selected as reference points. This gave -52.9, -53.2, -54.3, -54.3 kcal/mol, respectively. The fifth method used only the data on $\Delta_f H°(HX)$ and $\Delta_f H°(CH_3X)$ for Cl, Br, and I. They found $\Delta_f H°(CH_3F)_{est} = -54.7$ kcal/mol. Note that these last three values are within the combined uncertainties of our recommended value. The main difference between ref 1 and this work is their use of $\Delta_f H°(n\text{-PrF})$ and $\Delta_f H°(i\text{-PrF})$ as reference points.

TABLE 1: Differences between $\Delta_f H°(n\text{-PrX})$ and $\Delta_f H°(i\text{-PrX})$

X	V_x[a]	$\Delta_f H°(n\text{-PrX})$[b] (kcal/mol)	$\Delta_f H°(i\text{-PrX})$[b] (kcal/mol)	$\Delta\Delta_f H°$ (kcal/mol)
F	9.915	-68.3 ± 0.6 (-71.3 ± 1)[d]	-70.1 ± 0.4 (-76.2 ± 1)[d]	1.8 ± 0.7 (4.9 ± 1.4)[d]
OH	8.11	-61.0 ± 0.1	-65.1 ± 0.1	4.1 ± 0.2
Cl	7.04	-31.5 ± 0.3	-34.6 ± 0.3	3.1 ± 0.4
NH_2	6.67	-16.8 ± 0.1	-20.0 ± 0.2	3.2 ± 0.3
Br	6.13	-20.8 ± 0.8	-23.8 ± 0.6	3.0 ± 1.0
SH	5.77	-16.2 ± 0.2	-18.2 ± 0.2	2.0 ± 0.3
I	5.25	-7.2 ± 0.9	-9.6 ± 0.9	2.4 ± 1.3
CH_3	5.19	-30.0 ± 0.2	-32.1 ± 0.2	2.1 ± 0.3
H	2.70	-25.0 ± 0.1	-25.0 ± 0.1	0

[a] From ref 3. [b] Experimental values from ref 14. [c] $\Delta\Delta_f H = \Delta_f H°(n\text{-PrX})° - \Delta_f H°(i\text{-PrX})$. [d] Values estimated in this work, see text.

An earlier suggested value of $\Delta_f H°(MeF) = -59$ kcal/mol[17] is seen to be outside the range of any of the values estimated.

Appendix 1

An analysis of the difference between $\Delta_f H°(n\text{-PrX})$ and $\Delta_f H°(i\text{-PrX})$. In ref 1, $\Delta_f H°(MeF)$ was made by four methods, using $\Delta_f H°(n\text{-PrF})$ and $\Delta_f H°(i\text{-PrF})$ as reference points. We shall use two independent methods of examination: (1) consideration of the differences between $\Delta_f H°(n\text{-PrX})$ and $\Delta_f H°(i\text{-PrX})$ and (2) examination of the differences between $\Delta_f H°(R-OH, gas)$ and $\Delta_f H°(R-F, gas)$.

$\Delta_f H°(n\text{-PrX})$ and $\Delta_f H°(i\text{-PrX})$ and the difference $\Delta\Delta_f H$ have been listed in Table 1. Here X is F, OH, NH_2, SH, Cl, Br, CH_3, I, and H. All experimental data of $\Delta_f H°$ are taken from ref 14.

There are two reasons to doubt the reliability of data of $\Delta_f H°$ of n-PrF and i-PrF. $\Delta\Delta_f H$ is seen to increase in Table I with increasing electronegativity V_x. On basis of this tendency, the $\Delta\Delta_f H$ for X = F is estimated as about 5 kcal/mol. The value of 1.8 kcal/mol in Table 1 shows that the values of $\Delta_f H°$ (n-PrF) and $\Delta_f H°$ (i-PrF) are not self-consistent.

This conclusion is further supported by a comparison of $\Delta_f H°(RF)$ with $\Delta_f H°(ROH)$ for gas phase. F and OH form what has been called a "homothermal pair." These are substituents with similar sizes, electronegativities, and dipole moments.[18] When R is taken from a family with similar electronegativity such as ethyl, methyl, H, etc., the difference in heats of formation is usually a constant. Thus $\Delta_f H°(HOH,g) - \Delta_f H°(HF,g) = 7.5$ kcal/mol.[2] With $\Delta_f H°(CH_3OH) = -48.0$ kcal/mol, we might then estimate $\Delta_f H°(CH_3F) = -55.5$ kcal/mol in good agreement with our estimated value of $-55.9 \pm$ kcal/mol.

Applying this to n-PrF and i-PrF, we would conclude that

$$\Delta_f H°(n\text{-PrOH,g}) - \Delta_f H°(n\text{-PrF,g}) = \Delta_f H°(i\text{-PrOH,g}) - \Delta_f H°(i\text{-PrF,g})$$

or on rearrangement

$$\begin{aligned}\Delta_f H°(i\text{-PrF,g}) - \Delta_f H°(n\text{-PrF,g}) &= \Delta_f H°(i\text{-PrOH,g}) - \Delta_f H°(n\text{-PrOH,g})\\ &= 4.1 \pm 1\ \text{kcal/mol (Table 1)}\end{aligned}$$

These two approaches further support our conclusion that the data on $\Delta_f H°(n\text{-PrF})$ and $\Delta_f H°(i\text{-PrF})$ of ref 14 may be in error.

Using $\Delta_f H°(CH_3F)_{est} = -55.9 \pm 1$ kcal/mol and eq 5, we obtain

$$\Delta_f H°(EtF)_{est} = -66.3 \pm 1\ \text{kcal/mol}$$

$$\Delta_f H°(n\text{-PrF})_{est} = -71.3 \pm 1 \text{ kcal/mol}$$

$$\Delta_f H°(i\text{-PrF})_{est} = -76.2 \pm 1 \text{ kcal/mol}$$

$$\Delta_f H°(t\text{-BuF})_{est} = -89.9 \pm 1 \text{ kcal/mol}$$

These estimated values are consistent with our earliest work[4a] where the reference point for RF was selected as $\Delta_f H°(CH_3F) = -55.9$ kcal/mol take from ref 19. The difference between $\Delta_f H°(n\text{-PrF})_{est}$ and $\Delta_f H°(i\text{-PrF})_{est}$ in this work is 4.9 ± 1 kcal/mol. It is consistent with both the suggestion based on homothermal pairs[18] or the estimate based on Table 1.

Heats of formation for many other RF can be estimated following Figure 1.

Appendix 2

The differences between $\Delta_f H°$(R−OH,gas) and $\Delta_f H°$(R−F,gas). On the basis of ref 14 or Table 1, it was decided that the change from $\Delta_f H°$(R−OH,gas) to $\Delta_f H°$(R−F,gas) is

$$\Delta\Delta_f H°(n\text{-PrOH}/n\text{-PrF}) = \Delta_f H°(n\text{-PrOH}) - \Delta_f H°(n\text{-PrF}) = 7.3 \pm 0.7 \text{ kcal/mol}$$

$$\Delta\Delta_f H°(i\text{-PrOH}/i\text{-PrF}) = \Delta_f H°(i\text{-PrOH}) - \Delta_f H°(i\text{-PrF}) = 5.0 \pm 0.5 \text{ kcal/mol}$$

Liebman[20] assumed the change is about 6 kcal/mol. He used this value and $\Delta_f H°$(Me−OH,gas), −48.2 ± 0.1 kcal/mol, to predict $\Delta_f H°$(Me−F,gas). He obtained $\Delta_f H°(\text{Me−F,gas})_{est} = -54.3$ kcal/mol. The following analysis will show that his assumption is inaccurate.

Based on eq 5, this change is described as

$$\Delta\Delta_f H(\text{ROH/RF}) = \{\Delta_f H°(\text{Me−OH}) - \Delta_f H°(\text{Me−F})\} + \frac{m[(V_x(\text{F}) - V_x(\text{O})]}{0.67 \pm 0.21m} \quad (9)$$

The first term of the right side is a constant, 7.7 kcal/mol, but the second one is dependent upon m. Its value is 2.1, 3.3, or 4.2 kcal/mol for primary, secondary, or tertiary species, respectively. Such a rule works also for all RX species. For example, comparing the change from $\Delta_f H°(\text{R−OH})_{exp}$ to $\Delta_f H°(\text{R−SH})_{exp}$ or to $\Delta_f H°(\text{R−Cl})_{exp}$, we still see $\Delta\Delta_f H$(ROH/RSH) and $\Delta\Delta_f H$(ROH/RCl) are certainly dependent upon m, the degree of branching of species. From Table 1 and the above-stated estimate, we have

$$\Delta\Delta_f H°(n\text{-PrOH/nPrF})_{est} = 10.3 \text{ kcal/mol}$$

$$\Delta\Delta_f H°(i\text{-PrOH/iPrF})_{est} = 11.1 \text{ kcal/mol}$$

The data $\Delta_f H°(\text{R−OH})_{exp}$ are very reliable. We thus must carefully examine the reliability of $\Delta_f H°$ of n-PrF and i-PrF before taking them as reference points for thermochemical data.

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