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# COMMENTS

## Comment on "Heats of Formation of Alkyl Fluorides"

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The heats of formation of fluoroalkanes RF, for which reliable experimental data are sparse, have recently been the subject of some discussion.[1,2] The JANAF tables[3] quote a value for $\Delta_f H°$(MeF,g) of −234.3 ± 29 kJ mol$^{-1}$. Pedley,[4] in the most recent comprehensive compilation of thermochemical data for organic compounds, gives only heats of formation for *n*-PrF and *i*-PrF of −285.9 ± 2.2 and −293.5 ± 1.5 kJ mol$^{-1}$, respectively. Using the electronegativity scale of Luo and Benson,[5] Liebman et al.[1] sought to estimate $\Delta_f H°$(MeF,g) using the data for *n*-PrF and *i*-PrF as reference points; four schemes that relied upon these values gave heats of formation between −221 and −227 kJ mol$^{-1}$ for MeF, while another method gave −229 kJ mol$^{-1}$. Liebman et al. recommended a value of −225.4 ± 3.2 kJ mol$^{-1}$ for $\Delta_f H°$(MeF,g). Luo and Benson[2] have challenged these findings, mainly on the grounds that the experimental heats of formation for *n*-PrF and *i*-PrF are unreliable; their scheme predicts that [$\Delta_f H°$(*n*-PrF,g) − $\Delta_f H°$(*i*-PrF,g)] should be 20.5 ± 5.9 kJ mol$^{-1}$ compared with the experimental value of 7.6 ± 2.7 kJ mol$^{-1}$ from Pedley's tables.[4] On the basis of relationships between the heats of formation of EtX, $C_2H_3X$, and PhX, they were able to estimate $\Delta_f H°$(EtF,g), from which they deduced a value for $\Delta_f H°$(MeF,g), by appealing to a relationship between the difference [$\Delta_f H°$(MeX,g) − $\Delta_f H°$(RX,g)] and the covalent potential $V_x$ (or electronegativity). They also obtained $\Delta_f H$(MeF,g) from relationships between the heats of formation of MeX and HX; their recommended value for $\Delta_f H°$(MeF,g) is −233.9 ± 4.2 kJ mol$^{-1}$, close to that given in the JANAF tables.[3] Using the covalent potential $V_x$, Luo and Benson were able to estimate the heats of formation of EtF, *n*-PrF, *i*-PrF, and *t*-BuF. The purpose of this Comment is to show that an alternative bond energy scheme, using traditional Pauling electronegativities, leads to substantially similar conclusions concerning the heats of formation of fluoroalkanes, assuming the heat of formation of MeF to take the value proposed by Luo and Benson.

I have recently[6] applied the principle of electronegativity equilibration[7,8] to the calculation of the heats of formation of gaseous organic substances. It is postulated that in a series of alkane derivatives RX constant bond energy terms $E$(C−H) and $E$(C−X) can be derived; however, the term $E$(C−C) is variable according to eq 1:

$$E(\mathrm{C{-}C}) = E°(\mathrm{C{-}C}) + k|\Delta\chi| \qquad (1)$$

where $\Delta\chi$ is the difference between the group electronegativities of the groups linked by the C−C bond. The constant $k$ is found to be 72.4 kJ mol$^{-1}$, and $E°$(C−C) takes the value 348.12 kJ mol$^{-1}$. The group electronegativities are obtained from traditional Pauling atomic electronegativities[9] (H, 2.1; C, 2.5; F, 4.0; etc.) as explained in ref 6. For fluoroalkanes some relevant group electronegativities are collected in Table 1. Given the terms $E$(C−H) = 412.26 kJ mol$^{-1}$, $E°$(C−C) = 348.12 kJ mol$^{-1}$, and $k$ in eq 1 equal to 72.4 kJ mol$^{-1}$ as in ref 6, the difference [$\Delta_f H°$(*n*-PrF,g) − $\Delta_f H°$(*i*-PrF,g)] is calculated to be 20.4 kJ mol$^{-1}$, in excellent agreement with the value of 20.5 ± 5.9 kJ mol$^{-1}$ obtained by Luo and Benson.[2] Thus, I agree with Luo and Benson that the experimental heats of formation for *n*-PrF and *i*-PrF as quoted by Pedley[4] are somewhat suspect. Using the electronegativity equilibration scheme and taking the experimental values for *n*-PrF and *i*-PrF as anchor points, the term $E$(C−F) is found to be 437.4 kJ mol$^{-1}$ (from *n*-PrF) or 424.6 kJ mol$^{-1}$ (from *i*-PrF). These give seriously inconsistent values for $\Delta_f H°$(MeF,g) of −224.1 and −211.3 kJ mol$^{-1}$. If we accept the value of −233.9 ± 4.2 kJ mol$^{-1}$ proposed by Luo and Benson,[2] we can calculate the heats of formation of any fluoroalkane by the methods set out in ref 6, with $E$(C−F) = 447.2 kJ mol$^{-1}$. The results are compared with those obtained in ref 2 in Table 2. Also in Table 2 are estimates for EtF, *i*-PrF, and *t*-BuF made on the basis of Benson group terms derived from the most recent experimental calorimetric measurements on higher alkyl and aryl fluorides;[10] the value quoted for *n*-PrF in this column was obtained by adding the usual methylene increment of 20.6 kJ mol$^{-1}$ to the value for EtF. The three methods are in reasonably good agreement. The values from ref 10 in the third column of Table 2 may be considered to have a better experimental basis than the others; the mean deviation between these and the results of this work is 2.0 kJ mol$^{-1}$ compared with 2.6 kJ mol$^{-1}$ for the Luo−Benson estimates.[2] The figure of −89.9 kcal (−376.1 kJ) mol$^{-1}$ for the estimated heat of formation of *t*-BuF in ref 2 is clearly a misprint for −86.9 kcal (−363.6 kJ) mol$^{-1}$ as quoted elsewhere.[10,11] Slayden et al.,[12] on the basis of the figure of −225.4 kJ mol$^{-1}$ for the heat of formation of MeF,[1] obtained −351.1 kJ mol$^{-1}$ for *t*-BuF, which is in poor agreement with the values in Table 2, although the calculated difference [$\Delta_f H°$(MeF,g) − $\Delta_f H°$(*t*-BuF,g)] of 125.7 kJ mol$^{-1}$ agrees well with the estimate of 127.7 kJ mol$^{-1}$ in ref 2. The same authors[12] deduced $\Delta_f H°$(*t*-BuF,g) by another method that relied on the literature value for *i*-PrF; this gave −332.5 ± 6.9 kJ mol$^{-1}$ with a calculated difference [$\Delta_f H°$(*i*-PrF,g) − $\Delta_f H°$(*t*-BuF,g)] of 39.0

**TABLE 1: Group Electronegativities $\chi_R$ for Fluoroalkanes**

| R | $\chi_R$ | R | $\chi_R$ |
|---|---|---|---|
| Me | 2.2436 | $CH_2CH_2F$ | 2.3225 |
| Et | 2.2747 | CHMeF | 2.5356 |
| $CH_2F$ | 2.4970 | $CMe_2F$ | 2.5754 |

**TABLE 2: Calculated Heats of Formation of Fluoroalkanes (kJ mol$^{-1}$)**

| R | $-\Delta_f H°$(RF)[a] | $-\Delta_f H°$(RF)[b] | $-\Delta_f H°$(RF)[c] |
|---|---|---|---|
| Et | 272.2 | 277.4 ± 4.2 | 275.0 |
| *n*-Pr | 295.7 | 298.3 ± 4.2 | 295.6 |
| *i*-Pr | 316.1 | 318.8 ± 4.2 | 315.5 |
| *t*-Bu | 365.9 | 363.6 ± 4.2 | 361.6 |

[a] This work. [b] Reference 2. [c] Reference 10.

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kJ mol$^{-1}$, which is rather lower than the values of 45−50 kJ mol$^{-1}$ from the results in Table 2, but perhaps not very significantly after allowance for the uncertainties involved.

The conclusion to be drawn is that a bond energy scheme based on traditional Pauling electronegativities can give results comparable to those obtained from the Luo−Benson scheme, without the need to construct a new electronegativity scale. At the same time, the relationships developed by Luo and Benson are essential to the new estimate of $\Delta_f H°$(MeF,g); electronegativity equilibration methods are of no assistance here.

## References and Notes

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