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298 K enthalpies of formation of monofluorinated alkanes: theoretical predictions for methyl, ethyl, isopropyl and *tert*-butyl fluoride

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ABSTRACT: Experimentally measured 298 K enthalpies of formation are not well established for monofluoroalkanes. To supplement available experimental data, the multi-coefficient G3 (MCG3) quantum mechanical model has been applied to estimate this thermochemical quantity for methyl fluoride, ethyl fluoride, 2-fluoropropane (isopropyl fluoride) and 2-fluoro-2-methylpropane (*tert*-butyl fluoride). The following 298 K standard enthalpies of formation are suggested for these monofluoroalkanes: $\Delta H^\circ_{f,298}$ (MeF) $= -57.1 \pm 0.2$ kcal mol^{-1}, $\Delta H^\circ_{f,298}$ (EtF) $= -66.5 \pm 0.4$ kcal mol^{-1}, $\Delta H^\circ_{f,298}$ (*i*-PrF) $= -75.4 \pm 0.5$ kcal mol^{-1}, and $\Delta H^\circ_{f,298}$ (*t*-BuF) $= -86.0 \pm 2.0$ kcal mol^{-1} (1 kcal = 4.184 kJ). Copyright © 2004 John Wiley & Sons, Ltd.
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KEYWORDS: enthalpy of formation; fluoroalkanes; methyl fluoride; ethyl fluoride; isopropyl fluoride; *tert*-butyl fluoride

INTRODUCTION

Owing to their unique properties, interest in fluorinated compounds continues unabated. Their thermochemical properties, and in particular their standard enthalpies of formation, have been of key importance. However, as perusal of relevant review articles and book chapters shows,[1–4] the majority of research has been focused on species characterized by a very high degree of fluorination.

By contrast, very few contemporaneous experimental thermochemical studies address monofluorinated species.[5] Insofar as the effects of fluorine substitution are manifestly non-additive, we are thus missing key data for furthering our understanding of the energetics of organic compounds. For example, it is well accepted that the following reaction is significantly exothermic:[1–4]

$$4CH_3F \rightarrow 3CH_4 + CF_4$$

However, we are thwarted from knowing the exothermicity quantitatively because of the absence of enthalpy of formation data for methyl fluoride from the experimental calorimetric literature.

Even in those instances where the experimental literature has addressed monofluorinated alkanes, the results have been open to question with respect to their accuracy.[6–8] For example, there is only one measured enthalpy of formation for a *sec*-alkyl fluoride, that of isopropyl fluoride.[9] The value reported differs from that for the isomeric *n*-propyl fluoride by 1.8 ± 0.3 kcal mol^{-1} (1 kcal = 4.184 kJ).[10] This difference is substantially smaller than that observed for the corresponding isomeric amines (3.3 ± 0.1 kcal mol^{-1}), alcohols (4.2 ± 0.1 kcal mol^{-1}) and the other halides (Cl, 3.1 ± 0.3; Br, 3.0 ± 0.7; I, 2.4 ± 0.9 kcal mol^{-1}).[10]

Not only are enthalpies of formation rather rare in the literature for alkyl fluorides, but so too are enthalpies of reaction. Again, for those cases where data are available, there are troubling issues. For example, from an analysis of measured gas-phase dissociative protonation attachment reactions, Abboud *et al.*[11] asserted the halogen exchange reaction

$$1\text{-AdF} + HCl \rightarrow HF + 1\text{-AdCl}$$

(Ad = adamantyl) to have a Gibbs free energy change of -6.4 ± 2.8 kcal mol^{-1}. If we assume that the entropy change is negligible, the enthalpy of reaction is the same value (this entropy assumption seems reasonable, insofar as the entropy change for $MeF + HCl \rightarrow HF + MeCl$

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is −0.36 e.u.[12]). By contrast, using computationally derived enthalpies of formation for *t*-butyl fluoride (as discussed below) and archival values for the remaining species,[10] the related halogen exchange reaction

$$t\text{-BuF} + \text{HCl} \rightarrow \text{HF} + t\text{-BuCl}$$

is predicted to be essentially thermoneutral, with an enthalpy change of $0.2 \pm 1.9\,\text{kcal mol}^{-1}$. Why might these results be so discrepant? Perhaps *t*-butyl and 1-adamantyl are profoundly different in their response to fluorine substitution versus chlorine substitution. This seems unlikely, however. The ionization enthalpies for *t*-butyl fluoride and chloride and 1-adamantyl fluoride and chloride are known,[13] and the differences in ionization enthalpies for the two *t*-butyl and two 1-adamantyl halides are the same, within experimental error. Furthermore, if we accept that there might be expected to be a constant enthalpy change associated with replacing F by OH in a given monosubstituted fluoride, then we may also consider the reaction

$$1\text{-AdOH} + t\text{-BuCl} \rightarrow 1\text{-AdCl} + t\text{-BuOH}$$

Experiment[10,14] indicates this reaction also to be essentially thermoneutral ($\Delta H_{298} = 0.6 \pm 1.3\,\text{kcal mol}^{-1}$), suggesting that the proton-mediated fluoride–chloride exchange in the adamantyl system should be thermoneutral in spite of the analysis of Abboud *et al.*[11]

When experimental data are equivocal, estimation/correlation methods[5,7,15] and contemporary high-level quantum chemical calculations[8] can guide further analysis. We here apply such techniques with the specific goal of providing improved estimates of the 298 K standard enthalpies of formation for the four paradigmatic monofluoroalkanes, methyl fluoride, ethyl fluoride, 2-fluoropropane (isopropyl fluoride) and 2-fluoro-2-methylpropane (*tert*-butyl fluoride).

COMPUTATIONAL METHODS

Thermochemistry

The molecular geometries of all reactants (methyl fluoride **1**, ethyl fluoride **3**, isopropyl fluoride **5** and *tert*-butyl fluoride **7**), all heterolytic dissociation products derived therefrom (methyl cation **2a**, ethyl cation **4a**, isopropyl cation **6a** and *tert*-butyl cation **8a**), and all homolytic dissociation products derived therefrom (methyl radical **2b**, ethyl radical **4b**, isopropyl radical **6b** and *tert*-butyl radical **8b**) were optimized at the multi-coefficient quadratic configuration interaction including singles and doubles (MCQCISD)[16] level of theory. Vibrational frequency calculations at this same level were performed on **1**–**8** in order to assess the nature of various stationary points and to compute unscaled thermal contributions to the 298 K enthalpy.[17] The energies of **1**–**8**, the fluoride anion **9a** and fluorine atom **9b** and also the carbon **10** and hydrogen **11** atoms, were then computed at the multi-coefficient G3 (MCG3)[18,19] level, which has been demonstrated to predict enthalpies of activation, reaction and formation over large sets of molecules to a typical accuracy of $1\,\text{kcal mol}^{-1}$.[20] The MCG3 level of theory includes electron correlation effects through quadratic configuration interaction including singles, doubles and a perturbative estimate for triples [QCISD(T)][21,22] and employs basis sets of size up to an improved version of the 6–311++G(3d2f,2df,2p) basis set.[16,23]

$$\begin{array}{ccccc} \text{R—F} & \longrightarrow & \text{R}^+ & + & \text{F}^- \\ \mathbf{A} & & \mathbf{B} & & \mathbf{C} \end{array} \quad (1)$$

$$\begin{array}{ccccc} \text{R—F} & \longrightarrow & \text{R}^\bullet & + & \text{F}^\bullet \\ \mathbf{A} & & \mathbf{D} & & \mathbf{E} \end{array} \quad (2)$$

$$\begin{array}{ccccccc} \text{C}_m\text{H}_n\text{F} & \longrightarrow & \text{F} & + & m\text{C} & + & n\text{H} \\ \mathbf{A} & & \mathbf{E} & & \mathbf{F} & & \mathbf{G} \end{array} \quad (3)$$

The 298 K enthalpies of formation of the monofluorinated alkanes **1**, **3**, **5** and **7** were computed by three different approaches. These approaches differ primarily in the experimental data that are used as a foundation for the computational procedure. In each case, we compute 298 K enthalpies of reaction $\Delta H^\circ_{\text{r},298}$ for fragmentation of the alkyl fluorides into products for which experimental heats of formation have been reported. In the case of Eqn (1), the fragmentation is heterolytic and generates the fluoride anion and the alkyl cation. In the case of Eqn (2), the fragmentation is homolytic and generates the fluorine atom and the alkyl radical. Finally, in the case of Eqn (3), the fragmentation is the atomization reaction. With MCG3//MCQCISD computed enthalpies of reaction in hand, we may compute the heats of formation of the alkyl fluorides for the three cases by the following equations:

$$\Delta H^\circ_{\text{f},298}(\mathbf{A}) = \Delta H^\circ_{\text{f},298}(\mathbf{B}) + \Delta H^\circ_{\text{f},298}(\mathbf{C}) - \Delta H^\circ_{\text{r},298}(1) \quad (4)$$

$$\Delta H^\circ_{\text{f},298}(\mathbf{A}) = \Delta H^\circ_{\text{f},298}(\mathbf{D}) + \Delta H^\circ_{\text{f},298}(\mathbf{E}) - \Delta H^\circ_{\text{r},298}(2) \quad (5)$$

$$\Delta H^\circ_{\text{f},298}(\mathbf{A}) = \Delta H^\circ_{\text{f},298}(\mathbf{E}) + m\Delta H^\circ_{\text{f},298}(\mathbf{F}) + n\Delta H^\circ_{\text{f},298}(\mathbf{G}) - \Delta H^\circ_{\text{r},298}(3) \quad (6)$$

where all heats of formation on the right-hand side of Eqns (4)–(6) are taken from experiment and can be found in Table 1.

In addition to the MCG3//MCQCISD level of theory, density functional theory (DFT) calculations were carried

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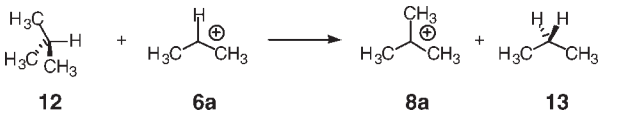
Table 1. Experimental 298 K standard enthalpies of formation for heterolysis, homolysis and atomization products found in Eqns (1)–(6)

Species		$\Delta H^\circ_{f,298}$	Ref.
CH_3^+	**2a**	261.8 ± 0.2	44
$CH_3^\cdot$	**2b**	35.1 ± 0.2	51
$C_2H_5^+$	**4a**	215.2 ± 0.5	45
$C_2H_5^\cdot$	**4b**	28.9 ± 0.4	52
iso-$C_3H_7^+$	**6a**	191.5 ± 0.9	44
iso-$C_3H_7^\cdot$	**6b**	22.0 ± 0.5	51
tert-$C_4H_9^+$	**8a**	167.3 ± 0.9	This study
tert-$C_4H_9^\cdot$	**8b**	12.8 ± 2	49
F^-	**9a**	-61.0 ± 1.3	See 8
F	**9b**	18.97 ± 0.072	50
C	**10**	171.29 ± 0.11	50
H	**11**	52.1 ± 0.001	50

out for all of the alkyl fluorides **1**, **3**, **5** and **7**, their respective alkyl cations **2a**, **4a**, **6a** and **8a**, the fluoride anion **9a**, isobutane **12** and propane **13**. Functionals employed were the gradient-corrected Hartree–Fock including[24] exchange functional of Becke[25] with the gradient-corrected correlation functional of Lee, Yang and Parr[26] (B3LYP) and the gradient-corrected Hartree–Fock including exchange and correlation functionals of Perdew and co-workers[27–29] as modified by Adamo and Barone[30] (*m*PW1PW91). For **1**–**9a** the *m*PW1N functional was also employed, this being a modification of *m*PW1PW91 that incorporates 40.6% Hartree–Fock exchange in place of the usual 25%.[8] All DFT calculations employed the 6–31+G(d) basis set.[31] Vibrational frequency calculations at both levels were performed to confirm all stationary points as minima and to compute unscaled thermal contributions to the 298 K enthalpy.[17]



(7)

One goal of the DFT equations was to use the isodesmic Eqn (7) to assess better the 298 K enthalpy of formation of **8a**, which was computed using the equation

$$\Delta H^\circ_{f,298}(\mathbf{8a}) = \Delta H^\circ_{r,298}(7) + \Delta H^\circ_{f,298}(\mathbf{12}) + \Delta H^\circ_{f,298}(\mathbf{6a}) - \Delta H^\circ_{f,298}(\mathbf{13}) \quad (8)$$

where experimental values for the 298 K standard enthalpies of formation of **12** and **13** were taken as -32.25 ± 0.14 and -24.92 ± 0.13 kcal mol^{-1}, respectively (each value is an average of two reported numbers[32]).

Software

MO and DFT calculations were carried out with the Gaussian 98 program suite.[33] Multicoefficient calculations employed the MULTILEVEL code.[34]

RESULTS AND DISCUSSION

Reactions

Heterolytic dissociation. At the MCQCISD level, geometry optimization proceeds by minimization of the gradient to the nearest stationary point.[17,35] For the majority of the species in this study, this process proceeded uneventfully, resulting in stationary point structures having all real vibrational frequencies (structures for all MCQCISD-optimized species may be found in the supplementary material). However, optimization of *tert*-butyl cation **8a** led to three different stationary points depending on the nature of the starting geometry. The lowest in energy at the MCG3 level, $\mathbf{8a_1}$, has C_s symmetry, the next lowest, $\mathbf{8a_2}$, has C_{3h} symmetry, and the highest in energy, $\mathbf{8a_3}$, has C_{3v} symmetry (Fig 1; note that symmetry was not *imposed* in any of the optimizations).

Energies of all species involved in heterolytic reactions at the MCQCISD and MCG3//MCQCISD levels are given in Table 2. Another level of theory is also presented, namely *m*PW1N,[8] which is a modification of the *m*PW1PW91 formalism that uses 40.6% Hartree–Fock exchange in place of the usual value of 25%; *m*PW1N is also defined to imply use of the 6–31+G(d) basis set. The *m*PW1N model was designed specifically for use in modeling halohydrocarbons and their nucleophilic substitution reactions. This level was examined to help resolve the issue of which one of the structures $\mathbf{8a_{1-3}}$ is the correct local minimum. At the MCQCISD level, all three structures are predicted to have one imaginary frequency each, of magnitudes 12, 62 and 193 cm^{-1}, respectively. The multilevel character of the model, however, makes it subject to some numerical noise, and thus the small magnitudes of the imaginary frequencies for $\mathbf{8a_1}$ and $\mathbf{8a_2}$ cannot be regarded as definitive. At the *m*PW1N level, $\mathbf{8a_1}$ is predicted to have *zero* imaginary frequencies (the frequency of lowest magnitude is 56 cm^{-1}), whereas $\mathbf{8a_2}$ and $\mathbf{8a_3}$ are predicted to have imaginary frequencies of magnitudes 37 and 192 cm^{-1}, respectively.

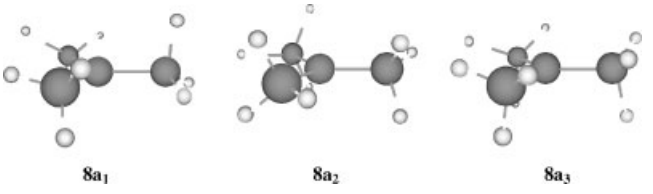


Figure 1. Ball-and-stick stereostructures for $\mathbf{8a_{1-3}}$ optimized at the MCQCISD level of theory

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Table 2. Absolute (E_h) [and relative (kcal mol^{-1})] energies, zero-point vibrational energies, and 298 K thermal contributions for **1**–**11** at various levels of theory

	Property			
*m*PW1N	E_{el}	ZPVE	$H_{298} - H_0$	H_{298}[a]
1	−139.712 68	0.039 81	0.003 85	−139.669 02
2a	−39.463 85	0.031 88	0.003 80	−39.428 18
3	−179.025 84	0.068 84	0.004 78	−178.952 23
4a	−78.837 11	0.061 82	0.004 09	−78.771 21
5	−218.338 52	0.097 09	0.005 97	−218.235 47
6a	−118.178 75	0.089 31	0.005 81	−118.083 63
7	−257.649 81	0.124 90	0.011 53	−257.517 62
8a$_1$	−157.513 22 [0.0]	0.117 99 [0.0]	0.007 25 [0.0]	−157.387 97 [0.0]
8a$_2$	−157.513 21 [0.0]	0.117 75 [−0.2]	0.006 51 [−0.5]	−157.388 96 [−0.6]
8a$_3$	−157.510 72 [1.6]	0.117 47 [−0.3]	0.005 94 [−0.8]	−157.387 31 [0.4]
9a	−99.827 66	0.000 00	0.002 36	−99.825 30
MCQCISD	E_{el}	ZPVE	$H_{298} - H_0$	H_{298}[a]
1	−140.132 30	0.039 27	0.003 86	−140.089 17
2a	−39.563 53	0.031 36	0.003 80	−39.528 37
2b	−39.924 61	0.029 72	0.003 97	−39.890 92
3	−179.538 96	0.066 80	0.004 93	−179.467 23
4a	−79.028 60	0.060 83	0.004 07	−78.963 70
4b	−79.327 28	0.059 27	0.004 86	−79.263 15
5	−218.946 98	0.095 57	0.005 98	−218.845 43
6a	−118.457 76	0.088 18	0.005 75	−118.363 83
6b	−118.732 21	0.087 92	0.005 96	−118.638 33
7	−258.355 51	0.122 84	0.007 37	−258.225 30
8a$_1$	−157.886 60 [0.0]	0.116 34 [0.0]	0.006 42 [0.0]	−157.763 84 [0.0]
8a$_2$	−157.886 38 [0.1]	0.115 91 [−0.3]	0.006 64 [0.1]	−157.763 83 [0.0]
8a$_3$	−157.884 03 [1.6]	0.115 83 [−0.3]	0.006 83 [0.3]	−157.761 36 [1.5]
8b	−158.138 41	0.116 20	0.007 12	−158.015 09
9a	−100.162 72	0.000 00	0.002 36	−100.160 36
9b	−100.021 58	0.000 00	0.002 36	−100.019 22
MCG3//MCQCISD	E_{el}			H_{298}[b]
1	−141.277 61			−141.234 48
2a	−39.890 20			−39.855 04
2b	−40.253 03			−40.219 34
3	−181.008 28			−180.936 55
4a	−79.680 61			−79.615 71
4b	−79.979 52			−79.915 39
5	−220.740 51			−220.638 96
6a	−119.433 88			−119.339 96
6b	−119.708 52			−119.614 64
7	−260.473 40			−260.343 19
8a$_1$	−159.186 88 [0.0]			−159.064 12 [0.0]
8a$_2$	−159.186 71 [0.1]			−159.064 16 [0.0]
8a$_3$	−159.184 37 [1.6]			−159.061 70 [1.5]
8b	−159.439 05			−159.315 73
9a	−100.975 19			−100.972 83
9b	−100.840 45			−100.838 09
10	−38.087 47			−38.085 11
11	−0.506 17			−0.503 81

[a] Sum of E_{el}, ZPVE and $H_{298} - H_0$.
[b] Sum of MCG3 E_{el} and MCQCISD ZPVE and $H_{298} - H_0$.

The *m*PW1N vibrational frequencies support assignment of **8a$_1$** as the local minimum and **8a$_2$** and **8a$_3$** as rotational transition-state structures for switching the identity of the unique methyl group in the C_s structure, in agreement with a previous study.[36] This vibrational analysis is curiously contrary to the energetic situation, where *m*PW1N predicts structure **8a$_2$** to be lower in 298 K enthalpy than **8a$_1$**. However, at the much more complete MCQCISD and MCG3//MCQCISD levels, **8a$_1$** and **8a$_2$** are predicted to be essentially degenerate, whereas **8a$_3$** is predicted to be 1.5 kcal mol^{-1} higher in energy. Taking all of these data together, it is clear that

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the potential energy surface for **8a** is fairly flat along the various rotational coordinates. In any case, from this point forward we will employ the data for $\mathbf{8a_1}$ in any calculation involving the *tert*-butyl cation.

A separate point meriting digression is the larger zero-point vibrational energy (ZPVE) computed for all structures at the *m*PW1N level compared with the MCQCISD. The vibrational frequencies for **7** and $\mathbf{8a_1}$ are listed in Tables 3 and 4, respectively. The larger frequencies predicted at the *m*PW1N level are consistent with it being a DFT level of theory incorporating a substantial fraction of Hartree–Fock exchange—such levels of theory typically require that their predicted frequencies be scaled by a factor somewhat less than 1.0 to bring them into better agreement with experiment.[17] Tables 3 and 4 also list the *m*PW1N scaled frequencies, using a scale factor of 0.9846. This factor minimizes the root mean square (r.m.s.) difference between the scaled frequencies and the MCQCISD frequencies for **7**. Note that in Table 4, this results in a lowest predicted frequency of 54.6 cm^{-1}

Table 3. Vibrational frequencies (cm^{-1}) for **7** computed at various levels of theory

Normal mode	MC-QCISD	*m*PW1N	Scaled *m*PW1N[a]
36	3127.5	3168.7	3119.8
35	3127.2	3168.7	3119.7
34	3126.4	3167.1	3118.3
33	3122.5	3164.3	3115.5
32	3118.6	3159.6	3110.9
31	3118.2	3159.6	3110.8
30	3043.0	3086.6	3038.9
29	3037.4	3079.1	3031.6
28	3037.0	3079.0	3031.5
27	1505.2	1545.4	1521.5
26	1483.8	1523.3	1499.8
25	1483.8	1522.8	1499.3
24	1471.6	1509.8	1486.5
23	1471.6	1509.5	1486.2
22	1454.2	1493.8	1470.7
21	1408.6	1450.8	1428.4
20	1390.8	1429.3	1407.3
19	1390.7	1428.6	1406.5
18	1285.9	1301.5	1281.5
17	1285.9	1301.2	1281.1
16	1219.0	1239.8	1220.6
15	1039.5	1058.8	1042.5
14	1039.4	1058.7	1042.4
13	952.0	971.8	956.8
12	921.3	935.6	921.2
11	921.2	934.3	919.9
10	917.2	912.6	898.6
9	763.2	765.0	753.2
8	453.5	459.5	452.4
7	453.3	458.8	451.7
6	397.4	409.5	403.2
5	330.7	334.5	329.4
4	330.6	334.0	328.9
3	256.3	256.8	252.9
2	255.7	255.1	251.1
1	181.1	189.3	186.3

[a] Scale factor = 0.9846.

Table 4. Vibrational frequencies (cm^{-1}) for $\mathbf{8a_1}$ computed at various levels of theory

Normal mode	MC-QCISD	*m*PW1N	scaled *m*PW1N[a]
33	3183.8	3216.4	3166.7
32	3177.6	3210.0	3160.4
31	3177.5	3209.0	3159.5
30	3098.7	3115.3	3067.3
29	3096.0	3114.4	3066.3
28	3083.1	3094.3	3046.5
27	2981.4	3027.0	2980.3
26	2959.7	3005.7	2959.3
25	2952.1	2999.4	2953.1
24	1506.3	1528.5	1504.9
23	1497.5	1523.7	1500.1
22	1490.1	1519.6	1496.1
21	1434.0	1461.8	1439.2
20	1418.9	1445.2	1422.9
19	1397.3	1435.0	1412.9
18	1360.8	1383.6	1362.3
17	1337.7	1372.1	1350.9
16	1328.6	1365.5	1344.4
15	1303.9	1326.6	1306.1
14	1295.3	1319.9	1299.5
13	1103.4	1125.9	1108.5
12	1014.3	1013.8	998.2
11	990.2	1001.9	986.4
10	974.4	990.5	975.3
9	838.7	842.0	829.0
8	748.3	786.2	774.0
7	707.7	761.9	750.1
6	435.8	451.3	444.3
5	400.1	407.2	400.9
4	396.4	406.2	400.0
3	205.4	189.8	186.9
2	119.3	87.7	86.4
1	11.8*i*	55.5	54.6

[a] Scale factor = 0.9846.

for $\mathbf{8a_1}$. This value has been used in place of the corresponding near-zero imaginary frequency computed at the MCQCISD level in computing the MCQCISD ZPVE and thermal enthalpic contributions listed in Table 2.

Whereas the values in Table 2 permit computation of the 298 K enthalpies of reaction for Eqn (1), in order to proceed to compute the 298 K enthalpies of formation for the alkyl fluorides **1**, **3**, **5** and **7** using Eqn (4), we must identify 298 K enthalpies of formation for the respective alkyl cations (**2a**, **4a**, **6a** and **8a**) and fluoride anion (**9a**). With respect to **9a**, the enthalpy of formation adopted (-61 ± 1.3 kcal mol^{-1}) is an average of seven experimental values listed in the NIST WebBook.[37–43] The error assigned to this value (determined as the r.m.s. of all reported experimental errors) is in excess of 1 kcal mol^{-1}, but this estimate would appear to be the best available.

As for the enthalpies of formation of the alkyl cations, the experimental values of 261.8 ± 0.2 and 191.5 ± 0.9 kcal mol^{-1} used for the methyl cation **2a** and the

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isopropyl cation **6a**, respectively, were taken directly from the NIST website[44] and are presumably calculated using the experimental enthalpies of formation of the appropriate alkyl radicals and their corresponding ionization energies, whereas the enthalpy of formation of 215.2 ± 0.5 kcal mol^{-1} applied for the ethyl cation **4a** comes from a recent measurement by Baer *et al.*[45] Some ambiguity exists in the literature for the enthalpy of formation of the *tert*-butyl cation **8a**, with reported values spanning a range from 165.8 to 171.0 kcal mol^{-1} and having typical error bars of the order of 1–2 kcal mol^{-1}.[46–48] In order to have a more precise value, we evaluated Eqn (7) at the B3LYP/6–31+G(d) and *m*PW1PW91/6–31+G(d) levels of theory, since trustworthy values for the 298 K enthalpies of formation for molecules **6–8** are available.[32,44] As Eqn (7) is an isodesmic equation, lower levels of theory are expected to benefit from substantial cancellation of errors in predicting the enthalpy of reaction. Absolute energies at both levels of theory for **6a**, **8a**, **12** and **13** are listed in Table 5. The 298 K enthalpy of reaction for Eqn (7) is predicted to be 16.8 and 16.9 kcal mol^{-1} at the B3LYP and *m*PW1PW91 levels, respectively. Employing either of these two closely agreeing numbers with the experimental 298 K enthalpies of formation for the remaining species according to Eqn (8) gives a predicted enthalpy of formation for **8a** of 167.3 ± 0.9 kcal mol^{-1}. This value is lower than estimates derived from the most recent work of Smith and Radom[48] (171 ± 2.4 kcal mol^{-1}) and Traeger and Kompe[47] (170.0 ± 0.6 kcal mol^{-1}). However, when our 167.3 ± 0.9 value for the enthalpy of formation of **8a** is used with the accepted ionization energy of 6.70 eV,[47] a value of 12.8 kcal mol^{-1} is obtained for the enthalpy of formation of the *tert*-butyl radical **8b**, and this is precisely in accordance with the most recent experimental measurement.[49]

Having established 298 K enthalpies of formation for the alkyl cations and fluoride anion, when Eqn (4) is used to compute the 298 K enthalpies of formation of the alkyl fluorides for the *m*PW1N, MCQCISD and MCG3// MCQCISD levels, the results for methyl fluoride **1** are −60.0, −50.5 and −54.4 kcal mol^{-1}, respectively, with an error of ±1.3 kcal mol^{-1}; the results for ethyl fluoride **3** are −69.0, −61.1 and -64.2 ± 1.4 kcal mol^{-1}; the results for isopropyl fluoride **5** are −74.2, −71.1 and -74.4 ± 1.6 kcal mol^{-1}; and the results for *tert*-butyl fluoride **7** are −84.7, −82.6 and -85.9 ± 1.6 kcal mol^{-1} (all errors are computed simply as the r.m.s. error in the experimental values for the relevant alkyl cation and the fluoride anion). Only the MCG3 level is specifically designed for high accuracy in thermochemical predictions, so the other two values are listed simply to provide an indication of how useful (or not) the other two levels may be considered to be for this purpose.

Table 5. 298 K enthalpies for **6a**, **8a**, **12** and **13** (absolute, E_h) and Eqn (7) (reaction, kcal mol^{-1}) at the B3LYP/6–31 + G(d) and *m*PW1PW91/6–31 + G(d) levels of theory

Target	B3LYP	*m*PW1PW91
6a	−118.118 25	−118.083 63
8a	−157.431 29	−157.388 00
12	−158.325 58	−158.282 88
13	−119.039 24	−119.005 43
Eqn (7)	16.8	16.9

Homolytic dissociation. At the MCQCISD level, optimization of each of the alkyl radicals **2b**, **4b**, **6b** and **8b** led to a single stationary point with zero imaginary frequencies. The starting geometry of **8b** was similar to the *tert*-butyl cation $\mathbf{8a_1}$ structure having C_s symmetry, but optimized to a structure resembling the *tert*-butyl cation $\mathbf{8a_3}$ structure having C_{3v} symmetry. Energies of the homolytic reaction products **2b**, **4b**, **6b** and **8b** and the fluorine atom **9b** at the MCQCISD and MCG3// MCQCISD levels are given in Table 2.

In contrast to the heterolytic reaction products, fairly reliable experimental 298 K enthalpies of formation are available for the homolytic reaction products. These values may be used to compute the 298 K enthalpies of formation for the alkyl fluorides **1**, **3**, **5** and **7** using Eqn (5), along with the values in Table 2 that permit computation of the 298 K enthalpies of reaction for Eqn (2). The enthalpy of formation used for the fluorine atom **9b** was obtained from the NIST–JANAF thermochemical tables.[50] As for the enthalpies of formation of the alkyl radicals, the experimental values of 35.1 ± 0.2 and 22.0 ± 0.5 kcal mol^{-1} used for the methyl radical **2b** and the isopropyl radical **6b**, respectively, were taken from a compilation by Tsang,[51] the enthalpy of formation of 28.9 ± 0.4 kcal mol^{-1} for the ethyl radical **4b** comes from a measurement by Seakins *et al.*[52] and the enthalpy of formation of 12.8 ± 2 kcal mol^{-1} applied for the *tert*-butyl radical **8b** comes from a recent measurement by Srinivasan *et al.*[49]

When Eqn (5) is used to compute the 298 K enthalpies of formation of the alkyl fluorides for the MCQCISD, and MCG3//MCQCISD levels, the results for methyl fluoride **1** are −58.2 and −57.0 kcal mol^{-1}, respectively, with an error of ± 0.2 kcal mol^{-1}; the results for ethyl fluoride **3** are −68.1 and -67.0 ± 0.4 kcal mol^{-1}; the results for isopropyl fluoride **5** are −76.9 and -75.9 ± 0.5 kcal mol^{-1}; and the results for *tert*-butyl fluoride **7** are −88.0 and -87.0 ± 2.0 kcal mol^{-1}.

Atomization energies. Energies and 298 K enthalpies of the atomization reaction products fluorine (^{2}P) **9b**, carbon (^{3}P) **10** and hydrogen (^{2}S) **11** computed at the MCG3 level are given in Table 2. These enthalpies were used to compute 298 K enthalpies of reaction for Eqn (3), which were subsequently used to compute the 298 K enthalpies of formation for the alkyl fluorides **1**, **3**, **5** and **7** using Eqn (6). The enthalpies of formation used in Eqn (6) for atomic fluorine **9b**,

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carbon **10** (171.29 ± 0.11 kcal mol^{-1}) and hydrogen **11** (52.103 ± 0.001 kcal mol^{-1}) were obtained from the NIST–JANAF thermochemical tables.[50]

When Eqn (6) is used to compute the 298 K enthalpies of formation of the alkyl fluorides for the MCG3 level of theory, the result for methyl fluoride **1** is -57.2 kcal mol^{-1}, the result for ethyl fluoride **3** is -65.9 kcal mol^{-1}, the result for isopropyl fluoride **5** is -74.9 kcal mol^{-1} and the result for *tert*-butyl fluoride **7** is -84.9 kcal mol^{-1}, each of which has an associated error of ± 0.13 kcal mol^{-1}.

Enthalpies of formation. In all cases except *tert*-butyl, the enthalpies of formation computed from homolytic dissociation and atomization [Eqns (5) and (6)] agree with one another to within about 1 kcal mol^{-1}. The agreement in the case of *tert*-butyl fluoride is within 2 kcal mol^{-1}, which is within the experimental error associated with the heat of formation of **8b**. Heats of formation computed from heterolysis [Eqn (4)] are in reasonably good agreement with the other two values for fluorides **5** and **7**, but fail to agree as closely for **1** and **3**. The disagreement for the last two cases may be associated with difficulties in accurately measuring (or computing) heats of formation for the highly unstable carbocations **2a** and **4a** compared with the more highly substituted and stable cations **6a** and **8a**. In any case, we consider the optimal estimates for the alkyl fluoride heats of formation to derive from taking an average of the values computed at the MCG3//MCQCISD level for only the homolytic and atomization processes, and the heterolytic results are provided here simply for comparison. On that basis, we recommend the following values for the enthalpies of formation of the monofluoroalkanes investigated in this study: $\Delta H^\circ_{f,298}$ (**1**) $= -57.1 \pm 0.2$ kcal mol^{-1}, $\Delta H^\circ_{f,298}$ (**3**) $= -66.5 \pm 0.4$ kcal mol^{-1}, $\Delta H^\circ_{f,298}$ (**5**) $= -75.4 \pm 0.5$ kcal mol^{-1} and $\Delta H^\circ_{f,298}$ (**7**) $= -86.0 \pm 2.0$ kcal mol^{-1} (the uncertainties are taken to be the largest r.m.s. error computed for either process).

Comparison of results. Our recommended enthalpies of formation for methyl, ethyl, isopropyl and *tert*-butyl fluoride are in reasonably good agreement with values recently suggested by Luo and Benson[7] and Smith[15] from an electronegativity-based analysis and with values obtained from the group additivity method of Schaffer[5] (Table 6). None of these values, however, are compatible with the values that would be estimated by use of the well-established corresponding alcohol enthalpies of formation[10] and the Benson[53]/Woolf[54–57]/Liebman[3,58] isothermal pair/thermochemical mimicry analysis, i.e. the assertion that there is a roughly constant 6 kcal mol^{-1} enthalpy of formation difference between a gas-phase species with a C—F bond and the isoelectronic, isosteric analog with a C—OH bond. That analysis would yield $-48 - 6 = -54$ kcal mol^{-1} for **1**,[32] $-56 - 6 = -62$ kcal mol^{-1} for **3**,[32] $-65 - 6 = -71$ kcal mol^{-1} for **5**[32] and $-75 - 6 = -81$ kcal mol^{-1} for **7**.[32] Of course, key to this analysis was the difference in the isomeric *n*- and isopropyl fluorides, which, as discussed earlier, are suspect. Using the values for the enthalpy of formation of the alkyl fluorides computed here and estimated from the other analyses noted above results in an average difference of ca 10 kcal mol^{-1} between the alkyl fluorides and the corresponding alcohols.

Table 6. Calculated 298 K enthalpies of formation for methyl fluoride (**1**), ethyl fluoride (**3**), isopropyl fluoride (**5**) and *tert*-butyl fluoride (**7**)

	$-\Delta H_f^\circ$ (kcal mol^{-1})			
Alkyl fluoride	This work	Luo and Benson[7]	Smith[15]	Schaffer *et al.*[5]
1	57.1 ± 0.2	55.9 ± 1		
3	66.5 ± 0.4	66.3 ± 1	65.1	65.7
5	75.4 ± 0.5	76.2 ± 1	75.5	75.4
7	86.0 ± 2.0	86.9 ± 1	87.5	86.4

Is the rule suspect, or is it perchance valid but with a different roughly constant difference? Schaffer *et al.*[5] reported the enthalpies of formation of 1-fluorononane, -dodecane and -tetradecane to be -101.2 ± 0.5, -116.9 ± 0.1 and -127.4 ± 0.2 kcal mol^{-1}, respectively. These three values are roughly internally consistent in terms of the 'universal methylene increment' of ca -4.9 kcal mol^{-1} per —CH_2— (see, for example, Ref. 59). The enthalpies of formation for the related alcohols are -90.0 ± 0.3 kcal mol^{-1} (summing the liquid enthalpy of formation[60] and the enthalpy of vaporization[61]), -104.3 ± 0.4 kcal mol^{-1} (summing the liquid enthalpy of formation[60] and the enthalpy of vaporization[61,62]) and -113.5 ± 0.6 kcal mol^{-1}.[63] It would appear that the difference in the enthalpy of formation of fluorides and the corresponding alcohol is closer to ca 12 than 6 kcal mol^{-1}. Moreover, it should be remembered that the 6 kcal mol^{-1} was generally derived by reference to C—F bonds involving carbons bonded to electronegative groups and/or sp^2 carbons, features that are expected to decrease the C—F/C—OH enthalpy of formation difference using the logic suggested by Kunkel *et al.*[58]

If we assert that there is essentially a constant difference for the enthalpies of formation of arbitrary alkyl fluorides and their corresponding alcohols, we can derive the following relationship:

$$\Delta H^\circ_{f,298}(R'F) = \Delta H^\circ_{f,298}(RF) + \left[\Delta H^\circ_{f,298}(R'OH) - \Delta H^\circ_{f,298}(ROH)\right] \quad (9)$$

for all alkyl groups R and R′. Letting R = *i*-Pr and R′ = *n*-Pr, we can derive the enthalpy of formation of *n*-propyl fluoride to be -71.2 ± 0.5 kcal mol^{-1} from our calculated enthalpy of formation of isopropyl fluoride, -75.4 ± 0.5 kcal mol^{-1}, and the archival enthalpies of formation of

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n-and isopropyl alcohol, -61.0 ± 0.1 and -65.2 ± 0.1 kcal mol^{-1}. Likewise, letting R = *t*-Bu and R′ = *n*-Bu, we can derive the enthalpy of formation of *n*-butyl fluoride to be -77.0 ± 2.0 kcal mol^{-1} from our calculated enthalpy of formation of *tert*-butyl fluoride, -86.0 ± 2.0 kcal mol^{-1}, and the archival enthalpies of formation of *n*- and *tert*-butyl alcohol, -65.7 ± 0.1 and -74.7 ± 0.2 kcal mol^{-1}. The resultant difference between *n*-propyl and *n*-butyl fluoride is -5.8 ± 2.1 kcal mol^{-1}, slightly larger than the -4.9 kcal mol^{-1} value associated with the 'universal methylene increment', but within the experimental error associated with our values.

Interestingly, there is a measurement in the literature for the enthalpy of ionization of *tert*-butyl fluoride, -27.3 ± 0.6 kcal mol^{-1}, that refers to the solution-phase value from reaction with SbF_5 in SO_2ClF at low temperature.[13] In the same paper, the corresponding values are available for some other alkyl fluorides and chlorides. Based on these data, and assuming complete ionization and cancellation of solvation effects for the organic halides, we would conclude that the difference in the heterolysis energies for any fluoride and the corresponding chloride would be roughly independent of the affixed alkyl group: for the isopropyl case the difference is -1.5 ± 1.1, for *tert*-butyl -1.9 ± 1.0, for 1-adamantyl -1.3 ± 1.2 and for *exo*-norbornyl -2.2 ± 1.1 kcal mol^{-1}. The same difference is also found for the *sec*-butyl case, at both -75 and -25 °C, corresponding to the cases where there is *not* and where there *is* rearrangement of the resulting *sec*-butyl carbocation to its *tert*-butyl isomer, namely -1.7 ± 1.2 and -2.0 ± 1.1 kcal mol^{-1}, respectively. This constancy suggests that there is essentially a constant difference between the enthalpy of formation of an arbitrary alkyl fluoride and the corresponding chloride and, in turn (and extrapolating further), between an alkyl fluoride and the corresponding alcohol.

There is an additional check of this analysis. A corollary of our analysis is that the difference in the ionization enthalpies of *sec*-butyl chloride at -25 °C (when it rearranges) and of *tert*-butyl chloride should be the difference of the enthalpy of formation of the two (liquid-phase) chlorides since the final product after ionization is the same. The difference in the reaction enthalpies is 4.6 ± 1.1 kcal mol^{-1}.[13] The difference in the enthalpies of formation of the two condensed-phase alkyl chlorides is 3.1 ± 0.7 kcal mol^{-1},[64] which is in acceptable agreement with our analysis. By the identical argument, the difference between the ionization enthalpies of *sec*-butyl fluoride at -25 °C (where it rearranges) and *tert*-butyl fluoride should be equal to the difference in the enthalpy of formation of the two (liquid-phase) fluorides. The difference of the reaction enthalpies is -4.7 ± 1.0 kcal mol^{-1}.[13] Making plausible estimates for the enthalpies of vaporization of the two species[65] results in the prediction that the difference of the *gas-phase* enthalpies should be -3.9 ± 1.0 kcal mol^{-1}. The same difference would be deduced for the corresponding alcohols under our assumption that the C—F/C—OH heat of formation difference is constant for all aliphatic fluorides and corresponding alcohols. Experimentally, the difference between the gas-phase enthalpies of formation of *sec*- and *tert*-butyl alcohol is -4.7 ± 1.2 kcal mol^{-1}, again in satisfactory agreement.

If on this basis we accept an ~ 12 kcal mol^{-1} difference between the enthalpy of formation for *n*-alkyl fluorides and their corresponding primary alcohols, and we apply it to *all* alkyl fluorides and their corresponding alcohols, we deduce enthalpies of formation of $-48 - 12 = -60$ kcal mol^{-1} for methyl fluoride **1**, $-56 - 12 = -68$ kcal mol^{-1} for ethyl fluoride **3**, $-65 - 12 = -77$ kcal mol^{-1} for isopropyl fluoride **5** and $-75 - 12 = -87$ kcal mol^{-1} for *tert*-butyl fluoride, results that are similar to those from our quantum chemical calculations but slightly more negative in every case, with the magnitude of the difference being 1–3 kcal mol^{-1}.

CONCLUSIONS

MCG3//MCQCISD quantum chemical calculations lend support to electronegativity-based and group additivity methods in predicting 298 K standard enthalpies of formation for monofluoroalkanes. Our predicted values of $\Delta H^\circ_{f,298}$ (**1**) $= -57.1 \pm 0.2$, $\Delta H^\circ_{f,298}$ (**3**) $= -66.5 \pm 0.4$, $\Delta H^\circ_{f,298}$ (**5**) $= -75.4 \pm 0.5$ kcal mol^{-1} and $\Delta H^\circ_{f,298}$ (**7**) $= -86.0 \pm 2.0$ kcal mol^{-1} assist in evaluating the utility of other predicted values [a referee, for instance, reports having used Eqn (6) to compute $\Delta H^\circ_{f,298}$ values for **1**, **3**, **5** and **7** of -56.4 ± 1.3, -65.0 ± 1.3, -74.8 ± 1.3 and -85.1 ± 1.3 kcal mol^{-1}, respectively, at the G3MP2B3 level.[66] The generally good agreement between these data and our benchmark values suggests that the less expensive G3MP2B3 level may prove useful for the prediction of enthalpies of formation for larger alkyl fluorides, where MCG3 calculations might become prohibitively demanding in terms of resources] and have also led to the conclusion that there is an empirical 10–12 kcal mol^{-1} difference between the computed enthalpies of formation of these monofluoroalkanes and their respective alcohols.

Supplementary material

MCQCISD optimized cartesian coordinates (Å) for **1**–**8** are available in Wiley Interscience.

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REFERENCES

1. Smart BE. In *Studies of Organic Molecules (Molecular Structure and Energetics)*, vol. 3, Liebman JF, Greenberg A (eds). VCH: New York, 1986; 141.
2. Kolesov VP, Kozina MP. *Russ. Chem. Rev.* 1986; **55**: 912.
3. Liebman JF. In *Fluorine-containing Molecules: Structure, Reactivity, Synthesis and Applications*, Liebman JF, Greenberg A, Dolbier WR Jr (eds). VCH: New York, 1988; 309.
4. Slayden SW, Liebman JF, Mallard WG. In *The Chemistry of Functional Groups. Supplement D2. The Chemistry of Organic Halides, Pseudohalides and Azides*, Patai S, Rappoport Z (eds). Wiley: Chichester, 1995; 361.
5. Schaffer F, Verevkin SP, Rieger HJ, Beckhaus HD, Rüchardt C. *Liebigs Ann. Chem.* 1997; 1333.
6. Liebman JF, Simões JAM, Slayden SW. *Struct. Chem.* 1995; **6**: 65.
7. Luo Y-R, Benson SW. *J. Phys. Chem. A* 1997; **101**: 3042.
8. Kormos BL, Cramer CJ. *J. Phys. Org. Chem.* 2002; **15**: 712.
9. Lacher JR, Kianpour A, Park JD. *J. Phys. Chem.* 1956; **60**: 1454.
10. Pedley JB, Naylor RD, Kirby SB. *Thermochemical Data of Organic Compounds* (2nd edn). Chapman and Hall: New York, 1986.
11. Abboud JLM, Notario R, Ballesteros E, Herreros M, Mo O, Yanez M, Elguero J, Boyer G, Claramunt R. *J. Am. Chem. Soc.* 1994; **116**: 2486.
12. Stull DR, Westrum EF Jr, Sinke GC. *The Chemical Thermodynamics of Organic Compounds*. Wiley: New York, 1969.
13. Arnett EM, Petro C. *J. Am. Chem. Soc.* 1978; **100**: 2563.
14. Flores H, Davalos JZ, Abboud JLM, Castaño O, Gomperts R, Jiménez P, Notario R, Roux MV. *J. Phys. Chem. A* 1999; **103**: 7555.
15. Smith DW. *J. Phys. Chem. A* 1998; **102**: 7086.
16. Fast PL, Truhlar DG. *J. Phys. Chem. A* 2000; **104**: 6111.
17. Cramer CJ. *Essentials of Computational Chemistry: Theories and Models*. Wiley: Chichester, 2002.
18. Tratz CM, Fast PL, Truhlar DG. *PhysChemComm* 1999; **2**: Article 14.
19. Fast PL, Sanchez ML, Truhlar DG. *Chem. Phys. Lett.* 1999; **306**: 407.
20. Fast PL, Schultz NE, Truhlar DG. *J. Phys. Chem. A* 2001; **105**: 4143.
21. Pople JA, Head-Gordon M, Raghavachari K. *J. Chem. Phys.* 1987; **87**: 5968.
22. Raghavachari K, Trucks GW, Pople JA, Head-Gordon M. *Chem. Phys. Lett.* 1989; **157**: 479.
23. Curtiss LA, Raghavachari K, Redfern PC, Rassolov V, Pople JA. *J. Chem. Phys.* 1998; **109**: 7764.
24. Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ. *J. Phys. Chem.* 1994; **98**: 11623.
25. Becke AD. *Phys. Rev. A* 1988; **38**: 3098.
26. Lee C, Yang W, Parr RG. *Phys. Rev. B* 1988; **37**: 785.
27. Perdew JP, Wang Y. *Phys. Rev. B* 1992; **45**: 13244.
28. Burke K, Ernzerhof M, Perdew JP. *Chem. Phys. Lett.* 1997; **265**: 115.
29. Burke K, Perdew JP, Wang Y. In *Electronic Density Functional Theory. Recent Progress and New Directions*, Dobson JF, Vignale G, Das MP (eds). Plenum Press: New York, 1998; 81.
30. Adamo C, Barone V. *Chem. Phys. Lett.* 1997; **274**: 242.
31. Hehre WJ, Radom L, Schleyer PvR, Pople JA. *Ab Initio Molecular Orbital Theory.* Wiley: New York, 1986.
32. Afeefy HY, Liebman JF, Stein SE. In *NIST Chemistry Webbook, NIST Standard Reference Database Number 69*, Linstrom PJ, Mallard WG (eds). National Institute of Standards and Technology: Gaithersburg, MD, 2003; http://webbook.nist.gov.
33. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Salvador P, Dannenberg JJ, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA. *Gaussian 98*. Gaussian: Pittsburgh, PA, 1998.
34. Rodgers JM, Lynch BJ, Fast PL, Zhao Y, Pu J, Chuang Y-Y, Truhlar DG. *MULTILEVEL*. University of Minnesota: Minneapolis, MN, 2002.
35. Schlegel HB. In *New Theoretical Concepts for Understanding Organic Reactions*, Bertrán J, Csizmadia IG (eds). Kluwer: Dordrecht, 1989; 33.
36. Sieber S, Buzek P, Schleyer PvR, Koch W, Carneiro JWdM. *J. Am. Chem. Soc.* 1993; **115**: 259.
37. Bierbaum VM, Schmitt RJ, DePuy CH, Mead RD, Schulz PA, Lineberger WC. *J. Am. Chem. Soc.* 1981; **103**: 6262.
38. Sorokin ID, Sidorov LN, Nikitin MI, Skokan EV. *Int. J. Mass Spectrom. Ion Processes* 1981; **41**: 45.
39. Kuznetsov SV, Korobov MV, Savinova LN, Sidorov LN. *Russ. J. Phys. Chem.* 1986; **60**: 766.
40. Sidorov LN, Borshchevskii AY, Boltalina OV, Sorokin ID, Skokan EV. *Int. J. Mass Spectrom. Ion Processes* 1986; **73**: 1.
41. Borshchevskii AY, Boltalina OV, Sorokin ID, Sidorov LN. *J. Chem. Thermodyn.* 1988; **20**: 523.
42. Blondel C, Cacciani P, Delsart C, Trainham R. *Phys. Rev. A* 1989; **40**: 3698.
43. Boltalina OV, Borshchevskii AY, Sidorov LN. *Russ. J. Phys. Chem.* 1992; **66**: 1223.
44. *NIST Chemistry WebBook; NIST Standard Reference Database*, Mallard WG, Linstrom PJ (eds). National Institute of Standards and Technology: Gaithersburg, MD, 2003: (http://webbook.nist.gov).
45. Baer T, Song Y, Liu J, Chen W, Ng CY. *Faraday Discuss.* 2000; **115**: 137.
46. Tsang W. *J. Am. Chem. Soc.* 1985; **107**: 2872.
47. Traeger JC, Kompe BM. In *Energetics of Organic Free Radicals*, Simões JAM, Greenberg A, Liebman JF (eds). Blackie: London, 1996; 59.
48. Smith BJ, Radom L. *J. Phys. Chem. A* 1998; **102**: 10787.
49. Srinivasan NK, Kiefer JH, Tranter RS. *J. Phys. Chem. A* 2003; **107**: 1532.
50. Chase MW Jr. *J. Phys. Chem. Ref. Data* 1998; Monograph No. 9.
51. Tsang W. In *Energetics of Organic Free Radicals*, Simões JAM, Greenberg A, Liebman JF (eds). Blackie: New York, 1996; 22.
52. Seakins PW, Pilling MJ, Niiranen JT, Gutman D, Krasnoperov LN. *J. Phys. Chem.* 1992; **96**: 9847.
53. Benson SW. *Chem. Rev.* 1978; **78**: 23.
54. Woolf AA. *J. Fluorine Chem.* 1978; **11**: 307.
55. Woolf AA. *Adv. Inorg. Chem. Radiochem.* 1981; **24**: 1.
56. Woolf AA. *J. Fluorine Chem.* 1982; **20**: 627.
57. Woolf AA. *J. Fluorine Chem.* 1986; **32**: 453.
58. Kunkel DL, Fant AD, Liebman JF. *J. Mol. Struct.* 1993; **300**: 509.
59. Cox JD, Pilcher G. *Thermochemistry of Organic and Organometallic Compounds*. Academic Press: London, 1970.
60. Mosselman C, Dekker H. *J. Chem. Soc., Faraday Trans.* 1975; 417.
61. Mansson M, Sellers P, Stridh G, Sunner S. *J. Chem. Thermodyn.* 1977; **9**: 91.
62. Svensson C. *J. Chem. Thermodyn.* 1979; **11**: 593.
63. Steele WV, Chirico RD, Nguyen A, Hossenlopp IA, Smith NK. In *DIPPR Data Series: Experimental Results for Phase Equilibria and Pure Component Properties*, vol. 1, Cunningham JR, Jones DK (eds). American Institute of Chemical Engineers: New York, 1991; 101.
64. He JA, An X, Hu R. *Acta Chim. Sin.* 1992; **50**: 961.
65. Chickos JS, Hesse DG, Liebman JF, Panshin SY. *J. Org. Chem.* 1988; **53**: 3424.
66. Baboul AG, Curtiss LA, Redfern PC, Raghavachari K. *J. Chem. Phys.* 1999; **110**: 7650.

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