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LETTERS

The Standard Enthalpy of Formation of the 1-Adamantyl Cation in the Gas Phase. An Experimental and ab Initio Re-assessment[||]

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The standard molar enthalpy of formation of gaseous 1-adamantyl chloride (**1**Cl,g) was determined experimentally by means of thermochemical techniques. Ab initio quantum-chemical calculations at the G2-(MP2) level were performed on adamantyl cation ($\mathbf{1}^+$) and on **1**Cl. Combination of these data with other experimental and computational results for adamantane (**1**H), isobutane (**2**H), *tert*-butyl cation ($\mathbf{2}^+$), and *tert*-butyl chloride (**2**Cl) provided purely experimental and purely computational, independent values for the standard enthalpy and Gibbs energy changes for reactions 1 and 2:

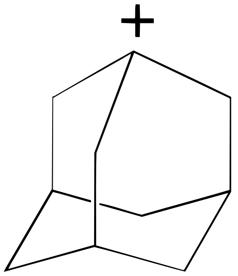
$$\mathbf{2}^+(g)+\mathbf{1}H(g)\rightleftarrows\mathbf{2}H(g)+\mathbf{1}^+(g) \quad \Delta H^\circ(1), \Delta G^\circ(1) \tag{1}$$

$$\mathbf{2}^+(g) + \mathbf{1}X(g) \rightleftarrows \mathbf{2}X(g) + \mathbf{1}^+(g) \quad \Delta H^\circ(2), \Delta G^\circ(2) \tag{2}$$

where X = Cl. This information was used to determine a value of 162.0 ± 2.0 kcal mol^{-1} for the standard molar enthalpy of formation of gaseous $\mathbf{1}^+$, $\Delta_f H^\circ_m(\mathbf{1}^+,g)$.

Holmes and co-workers[1] have recently used appearance energies to determine the standard enthalpy of formation of 1-adamantyl cation ($\mathbf{1}^+$) in the gas phase, $\Delta_f H^\circ_m(\mathbf{1}^+,g)$. The value they reported, 152 ± 3 kcal mol^{-1}, significantly differs from the values obtained by other methods (in the range 158−164 kcal mol^{-1}).[1] Inasmuch as carbocations are important chemical species,[2,3] this discrepancy has prompted us to reexamine the problem by means of experimental and computational techniques.

Equilibrium techniques, notably ICR (ion cyclotron resonance spectroscopy[4]), FT ICR (Fourier transform ion cyclotron



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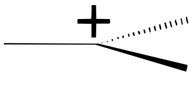

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TABLE 1: Experimentally Determined Standard Molar Energy of Combustion and Standard Molar Enthalpies of Combustion, Sublimation, and Formation in the Crystalline and Gaseous State at Temperature $T = 298.15$ K[a,b] of 1-Adamantyl Chloride

$\Delta_c U^{\circ}_{m}$[c]	−1398.92 ± 0.48
$\Delta_c H^{\circ}_{m}$[d]	−1401.00 ± 0.48
$\Delta_{sub} H^{\circ}_{m}$[e]	15.11 ± 0.17
$\Delta_f H^{\circ}_{m}$(cr)[f]	−57.55 ± 0.57
$\Delta_f H^{\circ}_{m}$(g)[g]	−42.45 ± 0.60

[a] All values in kcal/mol, (1 cal = 4.184 J). [b] This work. [c] Standard molar energy of combustion. [d] Standard molar enthalpy of combustion. [e] Standard molar enthalpy of sublimation. [f] Standard molar enthalpy of formation in the crystalline state. [g] Standard molar enthalpy of formation in the gaseous state.

resonance spectroscopy[5]), and HPMS (high-pressure mass spectrometry[6]) have been used to determine the standard enthalpy and Gibbs energy changes for the hydride and halide exchange reactions between (**1**$^+$,g) and *tert*-butyl cation (**2**$^+$,g) in the gas phase, reactions 1 and 2: where X = Cl, Br.

Reliable experimental $\Delta_f H^{\circ}_{m}$(g) values are presently available for adamantane (**1**H), isobutane (**2**H), and **2**$^+$.[7] In view of this, we have carried out the experimental determination of the standard enthalpy of formation of gaseous 1-adamantyl chloride, $\Delta_f H^{\circ}_{m}$(**1**Cl,g). *Combination of this datum with the other relevant experimental values involved in reaction 2 (X = Cl), leads to a new, purely experimental value of* $\Delta_f H^{\circ}_{m}$(**1**$^+$,g). This value can be usefully compared to that obtained using the experimental thermodynamic data involved in reaction 1.

High-level ab initio methodologies, particularly the G2[8] and G2(MP2)[9] treatments have been shown to yield values of the changes in thermodynamic state functions for chemical reactions agreeing within 0.1 eV (2.3 kcal mol^{-1}) with the experimental values. In the context of the present study, we thought it worthwhile to carry out the study of **1**H, **2**H, **1**Cl, **2**Cl, **1**$^+$, and **2**$^+$ at the G2(MP2) level. *This computational effort provides values of* $\Delta H^{\circ}(1)$, $\Delta G^{\circ}(1)$, *ΔH°(2, X = Cl) and ΔG°(2, X = Cl) fully independent from experiment.* They are used here in order to cross-check the experimental results.

$\Delta_f H^{\circ}_{m}$(**1**Cl,g) was determined in this work by combining the standard enthalpy of formation of crystalline **1**Cl, namely $\Delta_f H^{\circ}_{m}$(**1**Cl,cr), with its standard enthalpy of sublimation, $\Delta_{sub} H^{\circ}_{m}$(**1**Cl). $\Delta_f H^{\circ}_{m}$(**1**Cl,cr) was obtained by combustion calorimetry, using a rotary-bomb calorimeter.[10] $\Delta_{sub} H^{\circ}_{m}$(**1**Cl) was deduced from the temperature dependence of its vapor pressure (Clausius−Clapeyron)[11] over a 20 K temperature interval. The vapor pressure of the compound was measured by means of the Knudsen effusion technique.[11] Heat capacity measurements were carried out by differential scanning calorimetry.[12] Full experimental details are given as Supporting Information and Table 1 summarizes the results of the thermochemical study of **1**Cl.

Table 2 collects the results of the G2(MP2) calculations. Full details are also given as Supporting Material.

$\Delta_f H^{\circ}_{m}$(g) values taken from the literature[7,13] for adamantane, isobutane, *tert*-butyl chloride, and *tert*-butyl cation are, respectively, −32.0 ± 0.9, −32.25 ± 0.50, −42.99 ± 0.50, and 169.9 ± 0.9 kcal mol^{-1}. The results of the combination of these data are summarized in Tables 3 and 4.

Examination of these results leads to the following conclusions: (i) The agreement between the experimental and calculated changes in thermodynamic state functions for reactions 1 and 2 (X = Cl) is very good, particularly in the case of the Gibbs energies. Notice that these are the primary experimental data for these reactions, the enthalpy changes being obtained from the corresponding van't Hoff plots (experimental uncertainties estimated at ±1−2 kcal mol^{-1}).

TABLE 2: G2(MP2) Thermodynamic Functions, in Hartree, for All the Species Used in This Work

compound	H_{298}	G_{298}
1-adamantyl cation, **1**$^+$	−388.99432	−389.03284
adamantane, **1**H	−389.88158[a]	−389.91857
1-adamantyl chloride, **1**Cl	−849.03829	−849.07974
tert-butyl cation, **2**$^+$	−157.16933[b]	−157.20664[b]
isobutane, **2**H	−158.07400	−158.10855
tert-butyl chloride, **2**Cl	−617.22672[b]	−617.26407[b]

[a] Value taken from Castaño, O.; Notario, R.; Abboud, J.-L. M.; Gomperts, R.; Palmeiro, R.; Frutos, L. M. *J. Org. Chem.*, submitted. [b] Value taken from Abboud, J.-L. M.; Castaño, O.; Herreros, M.; Leito, I.; Notario, R.; Sak, K. *J. Org. Chem.* **1998**, *63*, 8995−8997.

TABLE 3: Determination of $\Delta_f H^{\circ}_{m}$(1$^+$,g) on the Basis of Reaction 1[a]

$\Delta G^{\circ}(1)$	$\Delta H^{\circ}(1)$	origin	$\Delta_f H^{\circ}_{m}$(**1**$^+$,g)[d]
−8.2 ± 0.1 (300 K)	−7.6 ± 1.0	HPMS[b]	162.6 ± 3.0
−10.2	−10.9	G2(MP2)[c]	159.3 ± 2.8

[a] All values in kcal mol^{-1}. [b] From ref 14. [c] This work. [d] Uncertainties taken as twice the standard deviation.

TABLE 4: Determination of $\Delta_f H^{\circ}_{m}$(1$^+$,g) on the Basis of Reaction 2[a]

ΔG°(2, X = Cl)	ΔH°(2, X = Cl)	origin	$\Delta_f H^{\circ}_{m}$(**1**$^+$,g)[f]
−5.9 ± 0.1 (600 K)	−6.3 ± 1.0	HPMS[b]	164.1 ± 3.2
−6.5 ± 1.0 (300 K)[c]			
−5.5 ± 0.4 (333 K)		FT ICR[d]	
−6.6 (298 K)	−8.4	G2(MP2)[e]	162.0 ± 2.4

[a] All values in kcal mol^{-1}. [b] From ref 14. [c] Calculated using the $\Delta H^{\circ}$and ΔS° values given in ref 14. [d] See ref 15. [e] This work. [f] Uncertainties taken as twice the standard deviation.

(ii) Using the G2(MP2) calculation on **1**Cl, we obtain a purely computational estimate of $\Delta_f H^{\circ}_{m}$(**1**Cl,g), namely, −44.7 kcal mol^{-1} found using atomization reaction and spin−orbit correction.[17]. This result compares favorably with the experimental value of − 42.5 kcal mol^{-1} found in this work.

(iii) The value of ΔG°(2, X = Cl) determined by FT ICR is quite consistent with that obtained by means of HPMS. This strongly supports the present treatment.

(iv) The average of the values of $\Delta_f H^{\circ}_{m}$(**1**$^+$,g) based on purely experimental data is 163.4 kcal mol^{-1}. The corresponding average based on the computed values of $\Delta H^{\circ}(1)$ and ΔH°(2, X = Cl) is 160.7 kcal mol^{-1}. These results are also consistent in view of the experimental uncertainties involved. We consider that the average of these data, 162.0 ± 2.0 kcal mol^{-1} can be taken as the final value of $\Delta_f H^{\circ}_{m}$(**1**$^+$,g) as determined by the methods indicated in this study.

(v) This result is significantly different from the value $\Delta_f H^{\circ}_{m}$(**1**$^+$,g) = 152 ± 3 kcal mol^{-1} reported in ref 1.

(vi) A referee has pointed out that the combination of $\Delta_f H^{\circ}_{m}$(**1**$^+$,g) = 162.0 kcal mol^{-1} with the available experimental ionization energy (determined by PES, photoelectron spectroscopy) of the 1-adamantyl radical (**1**•,g), namely, 6.21 eV[18] leads to a standard enthalpy of formation of gaseous **1**•, $\Delta_f H^{\circ}_{m}$(**1**•,g), of 19 kcal mol^{-1}. In turn, this makes the C(tertiary)−H bond dissociation energy in adamantane as high as 103 kcal mol^{-1}. This value is substantially larger than the corresponding value in **2**H, 95.9 kcal mol^{-1}.[19] On the other hand, the value 152 kcal mol^{-1} for $\Delta_f H^{\circ}_{m}$(**1**$^+$,g) leads to a dissociation energy of the C(tertiary)−H bond in **1**H of 96.3 kcal mol^{-1},[19] this result seeming physically more sound.

In view of the above, we have performed high-level ab initio calculations on **1**• and **2**•.[20] They do confirm the referee's contention that both C−H linkages have rather similar bond strengths. The situation is, however, more complicated. Thus, the value for $\Delta_f H^\circ_m(\mathbf{2}^+,g)$ currently accepted by NIST[7,21] and used here and in ref 1 is 169.9 kcal mol^{-1}. If we combine this datum with the value of $\Delta_f H^\circ_m(\mathbf{2}\cdot,g)$ of 11.0 kcal mol^{-1} [7] and the available PES ionization energies, namely, 6.70[7,22] and 6.58 eV,[7,23] we obtain bond strengths for the tertiary C−H bond in **2**H of 99.2 and 102.0 kcal mol^{-1}, respectively. Therefore, the criterion of the PE ionization energy of **1**· is to be considered with great circumspection.

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