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Calculation of Enthalpies of Formation of Secondary and Tertiary Aliphatic Carbenium Ions by Molecular Mechanics**

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Abstract: Steric energies (E_{st}) of carbenium ions, calculated by MM2, may be converted into enthalpies of formation (ΔH_f) by means of group increments. Increments of 204.7 kcal/mol for secondary and 187.4 kcal/mol for tertiary aliphatic carbenium ions, based on experimental ΔH_f values of 2-propyl (191.8 kcal/mol) and *tert*-butyl cation (166.2 kcal/mol) are proposed. The calculated ΔH_f values of eleven cations corrected for inductive effects due to β-alkyl substituents agree with experimental data.

We have recently developed empirical force-fields to calculate steric energies (E_{st}) of secondary[1] and tertiary[2] carbenium ions with molecular mechanics (MM2 program[3]). The force-field parameters were optimized in such a way that the strain changes occurring upon solvolysis of *p*-toluenesulfonates could be expressed in terms of steric energie difference (ΔE_{st}) between the substrate and the respective carbenium ion. Thus the parametrization is based on the transition structures for solvolysis rather than on carbenium ions. Although it is usually assumed[4] that the solvolysis reaction has a late transition state, which corresponds to similar structure and energy for transition state and intermediate, we have yet to show that our force-field parameters are indeed applicable to carbenium ions. This communication describes conversion of steric energies of carbenium ions into their enthalpies of formation (ΔH_f).

In the molecular mechanics approach enthalpies of formation of molecules are calculated from steric energies and bond or group increments[5]. For carbenium ions we propose a group increment of 204.7 for secondary and 187.4 for tertiary ions (Table 1). The usual values for CC- and CH-bonds incorporated in MM2 are retained as well as the translation-rotation term of 2.4 kcal/mol. The increments are arbitrarily selected such as to match the experimental enthalpies of formation of the 2-propyl (191.8 kcal/mol) and *tert*-butyl (166.2 kcal/mol) cations[6]. In addition, *Schleyer*'s β-branching corrections[7] of 3.0 for secondary and 1.5 kcal/mol for tertiary ions are used to account for inductive stabilization of the cations by alkyl substituents in β-position.

Table 1. Increments and β-branching corrections for calculation of ΔH_f of carbenium ions (kcal/mol).

Increment	*sec*	*tert*
Carbenium ion	204.7	187.4
β-branching	3.0	1.5

Most of the E_{st} values used for calculation of the data in Table 2 have been reported previously[1,2]. Comparison with exerimental enthalpies of formation shows satisfactory agreement in view of the variation of the experimental results from different groups. In particular, we note that the calculations reproduce the experimental energy difference of ca. 4 kcal/mol between the 2- and 1-adamantyl cation **11** and **12**[15] reasonably well, giving **11** 2.4 kcal/mol less stable than **12**. Since the force-field does not take into consideration electronic effects such as σ-bridging[17] the stability of the 2-norbornyl cation is underestimated by ca. 7 kcal/mol.

Correlation of the experimental versus calculated ΔH_f values affords a straight line with the equation:

$$\Delta H_f(\text{exp}) = 1.08\ \Delta H_f(\text{calc}) - 14.2;\ r = 0.997$$

The deviation of the slope from unity should not be considered significant since the latter is dominated by the value selected for the cyclobutyl cation (**3**). It decreases to 0.92 if the value of 213[11] is used

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Table 2. Calculated and experimental heats of formation of carbenium ions (kcal/mol).

Cation	ΔH_f(calc)	ΔH_f(exp)	Ref.
1 2-propyl	191.8[a]	191.8[a]	[6]
2 2-butyl	181.5	183	[8]
3 cyclobutyl	220.6	225 (213)	[9](11)
4 *tert*-butyl	166.2[a]	166.2[a]	[6]
5 cyclopentyl	186.4	188 (193)	[9](12)[b]
6 cyclohexyl	176.0	177	[9]
7 1-methyl-1-cyclopentyl	167.5	167 (169.4)	[12][b](13)
8 1-methyl-1-cyclohexyl	155.8	156.9 (160.4)	[11](13)
9 2-norbornyl	192.1	185	[14]
10 2-methyl-2-norbornyl	173.2	171	[12][b]
11 2-adamantyl	164.5	163	[15]
12 1-adamantyl	162.1	159 (160.7)	[15](16)

[a] Reference values. [b] ΔH_f (t-Bu$^{\oplus}$) corrected to 166 kcal/mol.

instead of 225[9]; with **3** excluded from the correlation the slope is 1.05.

The parametrization used here is tentative, and it may need further refinement once a more complete set of experimental data becomes available. We are particularly concerned about our crude treatment of inductive alkyl substituent effects. Recent data from gas-phase chemistry[14] and NMR studies under stable ion conditions[18] show that the positive charge must be extensively delocalized even in aliphatic ions. Our procedure of considering only β-inductive effects is clearly not satisfactory and it will have to be improved.

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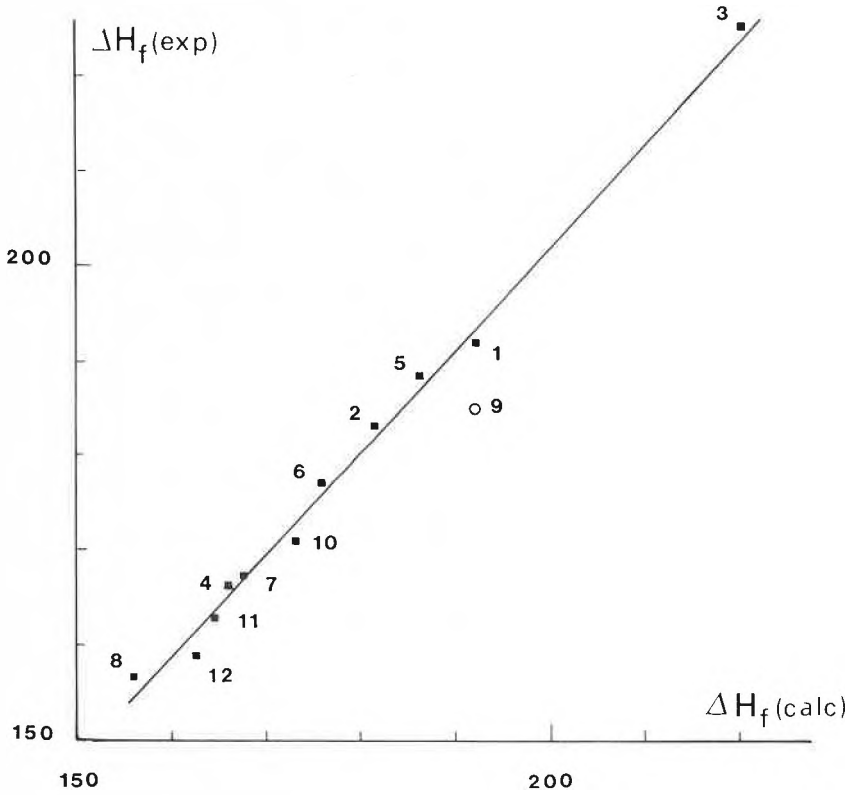

Fig. 1. Plot of ΔH_f (exp) vs. ΔH_f (calc) for carbenium ions.

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