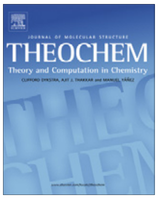
Journal of Molecular Structure: THEOCHEM 958 (2010) 76–81

Contents lists available at ScienceDirect

Journal of Molecular Structure: THEOCHEM

journal homepage: www.elsevier.com/locate/theochem



On quasi-tranferable molecular fragments. Part III: Parameters for use in pluri-fragment models

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ARTICLE INFO

Article history:
Received 17 June 2010
Accepted 21 July 2010
Available online 29 July 2010

Keywords:
Enthalpy of formation
Bond energies
Atomic charges
NMR chemical shifts

ABSTRACT

A simple formula for the standard enthalpy of perfect-gas molecules, $\Delta H_f^\circ = \sum_K \mathcal{F}(K) + \mathrm{ZPE} + H_T - H_0 - \sum_{k<l} \varepsilon_{kl} - \left(\mathrm{CNE} - E_{nb}^{KL}\right)$, is illustrated by novel applications and over 100 examples and comparisons with experimental results. The propounded model views molecules as constructs of chemical groups, K, L, . . . , etc. (such as CH_3, COOH, for example) characterized once and for all, independently of their belonging to one or another host, by fixed numbers $\mathcal{F}(K), \mathcal{F}(L), \ldots$, etc. ZPE + $H_T - H_0$ is the familiar sum of zero-point + heat-content energy, ε_{kl} is the intrinsic energy (at 0 K) of the bond connecting K and L, CNE (for Charge Neutralization Energy) takes care of the fact that K, L, . . . , are usually not electroneutral in the host molecule, and E_{nb}^{KL} measures nonbonded interactions summed over all pairs of groups K and L. New parameters, $\mathcal{F}[CH(X)]$ with X = CH_3, NH_2, OH, CHO, COOH, Cl, Br and SH, are described and an amazingly simple formula for carbon–hydrogen bonds, giving $\varepsilon_{CH}^* = \varepsilon_{CH} + \mathrm{CNE}$, turns out to be most useful any time a fragment CH(X) is bonded to one hydrogen atom at least.

1. Introduction

The mental partitioning of organic molecules into hypothetical fragments K, L, . . . , etc. has proven its merits in a simple approach aiming at the calculation of standard gas-phase enthalpies of formation, ΔH_f°. Each fragment, say CH_3, COOH, CH_2NH_2, . . . , for example, is described by a number $\mathcal{F}(K), \mathcal{F}(L), \ldots$, etc.—an energy contribution, in fact—which characterizes that group regardless of its location in one or another molecule. This certainly has the looks of brute-force theory.

The simplest model considers only two fragments, K and L, making up the molecule KL: its ΔH_f° is then [1]

$$\Delta H_f^\circ(KL) = \mathcal{F}(K) + \mathcal{F}(L) + Z(KL) - \varepsilon_{kl} - \mathrm{CNE} + E_{nb}^{KL} \qquad (1)$$

where $Z = Z(KL) = \mathrm{ZPE} + H_T - H_0$ is the familiar sum of zero-point + heat-content energies; $\varepsilon_{kl} = \varepsilon_{KL}$ is the intrinsic energy at 0 K of the bond formed by atoms $k(\in K)$ and $l(\in L)$. CNE, the so-called Charge Neutralization Energy, accounts for any possible charge transfer that may have occurred between K and L in the real molecule, and combines the energy increase of the electron donor with the energy lowering on the other side, which tends to keep CNE small to the point that CNE = 0 is an acceptable approximation in most cases. Finally, E_{nb}^{KL} stands for Coulomb nonbonded interactions between the atoms of K and those of L, not counting similar interactions within the fragments themselves.

The same reasoning leads to pluri-fragment models [2], with

$$\Delta H_f^\circ = \sum_K \mathcal{F}(K) + Z - \sum_{k<l} \varepsilon_{kl} - \left(\mathrm{CNE} - E_{nb}^{KL}\right) \qquad (2)$$

where E_{nb}^{KL} now collects all the nonbonded interactions between all those fragments K, L, . . . , etc. that are contemplated. Way down the line, "atoms-in-the-molecule" are the obvious ultimate subunits: this limit is equivalent to a bond-by-bond description, in which case the energy of atomization, ΔE_a^*, of molecules in their hypothetical vibrationless state at 0 K is given by [3,4]

$$\Delta E_a^* = \sum_{k<l} \varepsilon_{kl} - E_{nb} \qquad (3)$$

where E_{nb} is a small contribution reflecting all interactions between nonbonded atoms. The performance of the latter formulation is supported by nearly 250 comparisons with experimental data [3].

The description offered by Eq. (3) has an undeniable aura of conceptual simplicity—as long as one knows how to calculate all the ε_{kl}'s. The approximation CNE = 0 is not any longer involved. So, why bother with Eqs. (1) and (2)? The answer is: "for good practical reasons", owing to our inability, here and there, to get *all* the required bond energies; only a few of them are, indeed, needed in applications of Eqs. (1) and (2), provided the appropriate, invariant, usually easily accessible $\mathcal{F}$ terms are known. So we end up with admittedly approximate, but reasonable ΔH_f° results and

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doi:10.1016/j.theochem.2010.07.033

gain additional insight into what keeps atoms united in molecules. For the record, over 300 comparisons with experimental data support the philosophy embodied in Eqs. (1) and (2) [1,2].

Scope

Here we limit ourselves to fragments of the form $^{\cdot}CH(X)^{\cdot}$, with X = CH_3, NH_2, COOH,…, etc., to be inserted in chains of bonded atoms. The insertion of $^{\cdot}CH(OH)^{\cdot}$ between two carbons of propane, for example, yields 2-butanol: this strategy greatly facilitates the calculation of ΔH_f° since it avoids the CH, CO, and OH bonds that should otherwise be calculated for use in Eq. (3), the kind of simplification common to any fragment of this type.

2. The calculation of Z, $\mathcal{F}$, and ε_{kl}

2.1. The zero-point + heat-content energy

Vibrational energies in the harmonic oscillator approximation were deduced either from additivity rules [3,4] or from appropriately scaled Hartree–Fock (HF) frequencies. The 6-31G*(d) basis [5] was used in all cases. The scale factor f = 0.90139 applies to the frequencies of molecules containing only H, C and N, and f = 0.90015 applies to compounds containing oxygen as well. Additional factors are indicated as they occur.

2.2. The calculation of $\mathcal{F}$

The easiest approach towards the numerical evaluation of $\mathcal{F}[CH(X)]$ parameters is a matter of empirical trial and error applications of Eq. (2) to molecules K–[CH(X)]–L in which neither K nor L are single H atoms,

$$\Delta H_f^\circ = \mathcal{F}(K) + \mathcal{F}(L) + \mathcal{F}[CH(X)] + Z - \varepsilon_{K\mathcal{F}} - \varepsilon_{\mathcal{F}L} \tag{4}$$

where the ΔH_f°'s are taken at their experimental values. The presupposition is that $\mathcal{F}(K), \mathcal{F}(L)$ and Z are known beforehand and that one knows how to calculate the energies of the bonds linking K and L to CH(X). [Incidentally, the $\mathcal{F}(K), \mathcal{F}(L), \ldots$ parameters **1**–**34** of Table 1 were entirely deduced from theory based on bond energies, Eq. (3) [1].]

Table 1
Parameters $\mathcal{F}$ from Ref. [2] (**1**–**34**) and those (**12b** onwards) calculated here.[a]

	Formula	Radical	$\mathcal{F}$ (kcal/mol)
1	H	$H^{\cdot}$	50.61
9	CH_3	$CH_3^{\cdot}$	0.78
11	C_2H_3	$CH_2{=}CH^{\cdot}$	30.72
13	C_2H_5	$C_2H_5^{\cdot}$	–21.02
18	C_3H_7	n-$C_3H_7^{\cdot}$	–43.68
19		iso-$C_3H_7^{\cdot}$	–44.24
24	C_4H_9	n-$C_4H_9^{\cdot}$	–66.87
25		iso-$C_4H_9^{\cdot}$	–67.82
26		sec-$C_4H_9^{\cdot}$	–66.45
28	C_5H_{11}	n-$C_5H_{11}^{\cdot}$	–90.15
31	C_6H_5	$C_6H_5^{\cdot}$	5.47
34	C_7H_7	$C_6H_5CH_2^{\cdot}$	–24.24
12b	C_2H_4	$^{\cdot}CH(CH_3)^{\cdot}$	27.38
34a	CH_3N	$^{\cdot}CH(NH_2)^{\cdot}$	48.22
47a	CH_2O[b]	$^{\cdot}CH(OH)^{\cdot}$	9.44
49a	C_2H_2O	$^{\cdot}CH(CHO)^{\cdot}$	19.18
51a	C_2H_4O	$^{\cdot}CH(OCH_3)^{\cdot}$	–4.30
62a	$C_2H_2O_2$	$^{\cdot}CH(COOH)^{\cdot}$	–50.11
65a	CHCl	$^{\cdot}CH(Cl)^{\cdot}$	52.40
67a	CHBr	$^{\cdot}CH(Br)^{\cdot}$	62.36
70a	CH_2S	$^{\cdot}CH(SH)^{\cdot}$	60.94

[a] The numbering for **1**–**34** is that of Ref. [2]. For additional results, *cf.* Ref. [2]. The newly investigated radicals are inserted in that list with a momentary numbering from **12b** onwards.

[b] For neighboring CH(OH) fragments, use $\mathcal{F} = 4.55$ kcal/mol for each of them.

It is evidently desirable to profit by a sufficient number of test cases that could inform us as regards the scatter about the central (average) value of $\mathcal{F}[CH(X)]$ under the constraint $\mathrm{CNE} - E_{nb}^{KL} = 0$, but, of course, subsequent tests involving molecules in which K or L (or both) are hydrogen atoms are equally valuable inasmuch they further validate the approach propounded in Eq. (2).

The final problem now rests with the evaluation of the bond energies $\varepsilon_{K\mathcal{F}}$ and $\varepsilon_{\mathcal{F}L}$.

2.3. The calculation of ε_{kl}

The concept of bond energy was introduced by Fajans about 1920 and used to good effect by Pauling in "*The Nature of the Chemical Bond*". Many bond additivity schemes (involving large numbers of empirical parameters) have been devised since then, a fact that reveals the interest of chemists for this particular concept. Yet, conventional theoretical approaches, though offering insight into many relevant aspects regarding bond formation, failed to produce simple, accurate methods for calculating bond energies. As a result, the interest of chemists faded away and discussions of bond energies were more often than not kept at a semi-quantitative level. But things have evolved [3,4]: the more recent formula describing the energy of chemical bonds in ground-state molecules—the so-called *intrinsic bond energy*—translates intuitive expectations, namely, that the energy of a chemical bond formed by atoms k and l should depend on the amount of electronic charge carried by these atoms. Because of the important role played by atomic charges, great attention is given to the latter.

In this work we consider carbon–carbon bonds and take advantage of accurate linear correlations between ^{13}C NMR chemical shifts, δ_C (from TMS), and net atomic charges, q_C. For typical alkane carbons it is [3]

$$q_C = -0.148(\delta_C - \delta_C^{C_2H_6}) + 35.1 \text{ me} \tag{5}$$

where $\delta_C - \delta_C^{C_2H_6}$ is the NMR shift relative to ethane. (With the results of Ref. [6] it appears that $\delta_C^{C_2H_6} = 5.85$ ppm from TMS is a reasonable selection.) This formula also applies to carbons bonded to nitrogen (in amines), but not to carbons attached to oxygen. For the latter (ethers and alcohols) use

$$q_C = -0.148(\delta_C - 65.9) + 31.26 \text{ me} \tag{6}$$

where δ_C is the carbon shift relative to tetramethylsilane (TMS). For olefinic sp^2 carbons, on the other hand, use

$$q_C = 0.15(\delta_C - 122.8) + 7.7 \text{ me} \tag{7}$$

Finally we get the energies of $C(sp^3)$–$C(sp^3)$ bonds

$$\varepsilon_{CC} = 103.891 - 0.488 q_{C_k} - 0.488 q_{C_l} \text{ kcal/mol} \tag{8}$$

and those of $C_k(sp^3)$–$C_l(sp^2)$ bonds, namely,

$$\varepsilon_{CC} = 92.68 - 0.488 q_{C_k} + 0.275 q_{C_l} \text{ kcal/mol} \tag{9}$$

Now, what about the carbon-hydrogen bonds?

They also depend on the charges of the bond-forming atoms, e.g.,

$$\varepsilon_{CH} = 108.081 - 0.247 q_C - 0.632 q_H \text{ kcal/mol}$$

for typical $C(sp^3)$–H bonds. This formula is rightfully used in applications of Eq. (3), i.e., under conditions which do not know of any CNE term. But there is an important reservation if one wishes to single out H as a fragment with $\mathcal{F} = 50.61$ kcal/mol: the accompanying charge neutralization is far from being negligible, as revealed by direct calculations [3,4]. In return, we benefit from a fortunate circumstance: $\varepsilon_{CH}^* = \varepsilon_{CH} + \mathrm{CNE}$ is nearly constant, about 98–99 kcal/mol for