

Estimation of Enthalpies of Formation of Highly Reactive Organic Compounds

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Summary: A simplified scheme of atom equivalents to relate ab initio total electronic energies at the 6-31G* basis set level to enthalpies of formation is applied to free radicals and classical carbocations. The estimations are quite satisfactory and the average errors are similar to experimental uncertainties as well as to other theoretically determined values. Some possible further extensions of the method are pointed out.

Introduction

Since long ago chemists have firmly and methodically turned their way of considering chemical compounds from a macroscopic standpoint (chemical and physical properties) to a structural one (chemical bonds, topology, conformations, isomers, etc.). Thus, chemical structures have become nearly the universal and natural language in analysing the nowadays huge number of chemical species.

At present, a standard chemist interested in looking for the structure and reactivity of any (existing or hypothetical) compound can resort to his usual computational facilities, input some minimum number of atomic and topological molecular parameters and to choose the suitable software to solve the stationary Schrodinger equation in order to calculate the molecular electronic structure. This excellent state of affairs leads us to inquire about the existing agreement between theoretical results and experimental data. The question is too broad to be able to give a precise and definite answer. Since the three-bodies problem cannot be solved analytically in classical mechanics, one can hardly hope to get a closed solution for the many body (nuclei and electrons) molecular quantum mechanics equation.

Thus, one is forced to resort to approximations which depend upon the results that are sought after. It is a well known fact that a given method yielding satisfactory results for a specific property may do poorly or even fail for other ones. Then, one must restrict oneself to deal with

reduced set of properties and to apply suitable methods to study them.

Heats (or enthalpies) of formation is the subject of this article and it is well known that the most important practical application of this thermodynamic property is to explore chemical reactivities and equilibria. In this regards, it is important to have a sufficiently accurate method for predicting enthalpies of formation.

Any of the existing first principle methods cannot estimate heats of formation for medium size molecules within sensible uncertainty limits (i.e. less than 2 kcal/mol) [1] so that one must turn to combined procedures seeking for chemical accuracy. The atom equivalents methods for relating ab initio energies to enthalpies of formation has shown to yield enough satisfactory results [2]. This method combines ab initio total molecular energies at different basis set levels with empirical atom equivalents via a quite simple calculation scheme to obtain enthalpies of formation.

Yala [3] developed another alternative scheme by using the linear-regression method on the basis of the precedent procedure to reduce the number of atomic parameters and got a similar accuracy degree when computing heats of formation as that obtained by Ibrahim and Schleyer [2]. However, this scheme presented some deficiencies which were overcome later on by the present author [4] without any reduction in accuracy.

The simplified scheme for relating *ab initio* energies to enthalpies of formation resorted to only 14 parameters which were employed to analyse 62 standard sample molecules [4]. The calculated heats of formation compared fairly well with the experimental data and other theoretically determined values.

The aim of this paper is to extend the method to deal with highly reactive organic compounds, such as free radicals and classical carbocations. The structure of the paper is as follows: first, the method is presented and the introduction of the necessary parameters for radicals and carbocations is discussed. Then, the numerical results are given and compared with other theoretical estimations and available experimental data. Finally, the significant features of this simplified procedure of atom equivalents is discussed, paying special attention to the comparison with other similar related schemes. Some possible further applications and extensions of the method are pointed out in order to calculate other physical chemistry properties.

Results and Discussion

Table-1 lists atom equivalents for carbon, nitrogen and hydrogen at the 6-31G* basis set level employed in this paper. Although Ibrahim and

Table-1: Atom equivalents for carbon, nitrogen and hydrogen at the 6-31G* basis set level.

Atom	Coordination number/s	Atom equivalent (a.u)
C	4	-37.88685
	3	-37.88439
	2	-37.88371
N	3	-54.46909
H-(C)	1	-0.56967
C.	2,3,4	-37.90364
C-(C.)	2,3,4	-37.88712
C+	2,3,4	-37.92884
C-(C+)	2,3,4	-37.88352

Schleyer defined atom equivalents at 3-21G and 6-31G* basis set levels, the results for the first set were not totally satisfactory since they failed to correlate the experimental and the calculated enthalpies of formation in some set of molecules, such as strained hydrocarbons. This feature is due to the fact that basis sets with polarization functions (such as 6-31G*) are known to be needed to describe the energies of molecules where electron correlation corrections are significant, while 3-21G basis set does not include such functions. Thus, only atom equivalents at the 6-31G* basis set level were selected [4].

Table-2 shows results for experimental and calculated heats of formation for free radicals whereas Table-3 presents similar results for classical carbocations. Previous theoretical estimations are adjoined for comparative purposes. The enthalpies of formation for these sets of highly reactive chemical species show a very good agreement with available experimental data and a similar degree of accuracy to the other equivalent theoretical procedure. However, present results are derived on the basis of a significantly smaller number of atomic equivalents and besides they were not fitted against experimental data on heats of formation. The only large disagreement for free radicals is for *tert*-butyl which is equal to that found by Ibrahim and Schleyer. It is hardly surprising because this is a very strained molecule, although it could be that the experimental value is erroneous. Regarding carbocations, results are quite satisfactory. Although average deviations are larger than those for free radicals, one must take into account that heats of formation are rather great quantities so that minor errors in the estimations convey relatively large disagreements between experimental and theoretical results.

Table-2: Results of atom equivalents analysis for free radicals

Formula	Radical	-E(HF 6-31G*) (a.u.)	Exp.ΔH _f ^o (g) (kcal/mol) (a)	Calc. ΔH _f ^o (g) (kcal/mol)		Difference	
				Ref.2	This work	Ref.2	This work
CH ₃	Methyl	39.55899	35.1	33.7	33.7	-1.4	-1.4
CH ₄ N	Aminoethyl	94.58673	35.7	36.2	36.4	+0.5	+0.7
C ₂ H	Ethynyl	76.15009	135.0	132.0	132.0	-3.0	-3.0
C ₂ H ₃	Vinyl	77.39029	70.4	68.7	68.7	-1.7	-1.7
C ₂ H ₅	Ethyl	78.59715	25.99	26.3	26.3	+0.4	+0.4
C ₃ H ₇	<i>n</i> -Propyl	117.63144	21.0	22.8	21.3	+1.8	+0.3
C ₃ H ₇	Isopropyl	117.63438	18.2	19.6	19.6	+1.4	+1.4
C ₄ H ₉	<i>ter</i> -butyl	156.67051	8.7	13.5	13.5	+4.8	+4.8

Average error (kcal/mol): Ref.2: 1.9. This work: 1.7. (a) McMillen, D.F. and D.M. Golden, *Ann. Rev. Phys. Chem.*, **33**, 493 (1982).

Table-3: Results of atom equivalents for classical carbocations

Formula	Carbocation	-E(HF 6.31G+) (a.u)	Exp. ΔH_f° (g) (kcal/mol)	Calc. ΔH_f° (g) (kcal/mol)		Difference	
				Ref.2	This work	Ref. 2	This work
CH ₃	Methyl	39.2304	261 (a)	256	256	-5	-5
C ₂ H ₅	Vinyl	77.08673	266.9 (b)	273	273	+6.1	+6.1
C ₂ H ₅	Ethyl	78.31123	215.6 (c)	219	219	+3.4	+3.4
C ₃ H ₅	Cyclopropenyl	115.00702	256 (a)	250	250	-6	-6
C ₃ H ₅	Propargyl	114.95110	281 (a)	285	287	+4	+6
C ₃ H ₅	Allylic	116.19321	255 (c)	222	222	-3	-3
C ₃ H ₇	Isopropyl	117.38076	191 (c)	190	192	-1	+1
C ₄ H ₉	sec-Butyl	156.42081	183 (c)	183	181	0	-2
C ₄ H ₉	tert-butyl	156.44241	166 (c)	166	166	0	0
C ₅ H ₉	Cyclopentyl	194.29211	191 (d)	192	191	+1	0

Average error (kcal/mol): Ref. 2: 3.0. This work: 3.3.

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(c) Rosenstock, H.M. Draxl, K., Steiner, B.W., and Herron, J.T., 1977, *J. Phys. Chem. Ref. Data*, Vol. 6, Suppl. 1.

(d) Allinger, N.L., Dodziuk, H. Rogers, D.W., and Naik, S.N., 1982, *Tetrahedron*, 38, 1593.

The average errors for free radicals and classical carbocations (1.7 and 3.3 kcal/mol, respectively) are similar to the experimental uncertainties, so that they make up suitable predictors. The benefit of this sort of calculation based on a simplified scheme of atom equivalents is in line with other previous results for different sort of molecules [4-6].

When dealing with the theoretical estimation of heats of formation one looks for procedures relying less dependence on experimental data, less computational work and much on first principles. Some attempts along these lines have been advanced but results and pretended ab initio procedures were not satisfactory at all [7]. Consequently, one must reach some sort of equilibrium between different requirements in order to have a practical and simple way to relate ab initio to experimental energies and thus to take benefit of the impressively large set of first principles data for a wide variety of chemical species. The simplified scheme of atom equivalents to relate ab initio energies (at the 6-31G* basis set level) to enthalpies of formation is one of these methods. We have shown via a transparent illustrative example the manner to apply the procedure. The results displayed for free radicals and classical carbonocations enlarge the set of molecules calculated with this method and the degree of accuracy is totally satisfactory since the average errors are the same as experimental uncertainties, so that a better agreement can hardly be demanded to the estimation.

Hence, this set of atom equivalents can be used with confidence for the conversion of ab initio total electronic energies at the 6-31G* basis set level into enthalpies of formation for free radicals and carbocations.

A possible extension of the method is to apply it to other sort of molecules, such as protonated species, inorganic compounds, large organic polyenes, benzenoid hydrocarbons, etc. Besides, it should be interesting to resort to data obtained at electronic correlated levels to define new atoms equivalents and thus to extend the study of systems with extended electron delocalization, aromatic and electron deficient systems, transition structures, etc., where electronic correlation is significant. Work along these lines in being carried out in the laboratory and results will be published elsewhere in the near future.

Experimental

The large number of ab initio results for a wide variety of molecules, ions and radicals offers a chemist the unvaluable chance to compute at a first principles level the electronic properties of many species for which no experimental values are available and/or they are doubtful [8-10]. The enthalpy of formation is a basic state function which is closely related to the understanding of the chemical bond.

There exist two principal methods for calculating heats of formation [11]. The first one

uses the molecule in a particular sort of chemical reaction, such as anisodesmic (retention of number of bonds of each type, i.e. bond separation reaction), homodesmic (isodesmic + retention of atomic environment), hydrogenation, isogyric (retention of number of unpaired spins) or atomization reaction [7]. Then, the experimental heats of formation of the remaining reactants and products are combined with the computed heat of reaction via Hess law to provide the unknown enthalpy of formation.

The second method employs the concept of atom or group equivalents [12,13] which are assigned atomic or group electronic energies for the calculation of the heat of formation. The procedure gives a model electronic energy which can be transformed into the standard enthalpy of formation ΔH_f° through the simple formula

$$\Delta H_f^\circ = E_{el} - \sum_r k_r b_r \quad (1)$$

where E_{el} is the total molecular electronic energy, k_r is the number of atoms or groups of each sort and b_r is the corresponding atom or group equivalent. Ibrahim and Schleyer [2] developed a set of 56 atomic equivalents for H, C, N, O and F atoms involving a variety of small inorganic and organic molecules including fluorocarbons, free radicals, carbocations and protonated species. Later on, Yala [3] contracted such a set to just 11 parameters but he did not consider free radicals, classical carbocations and protonated species. My 14 optimized atom equivalents for H, C, N, O, F, and Cl atoms [4] were tested for the same set of molecules as chosen by Yala. The three methods yield rather satisfactory estimation of heats of formation.

In order to extend the test of the simplified scheme of atom equivalents [4], here the highly reactive free radicals and carbocation species chosen by Ibrahim and Schleyer are included (see Tables 6 and 7 in Ref. 2). Then, atom equivalents at the 6-31G* basis set level (See Table -1 in Ref. 4) must be completed with four additional carbon equivalents which are necessary to transform the ab initio total electronic energies of carbocations and free radicals into heats of formation. One equivalent for the carbon carries the positive charge (C+) or the odd electron (C.) and the other two, C-(C+) and (C.), are used for the attached carbon(s). The atom equivalents were taken from

Ibrahim and Schleyer's compilation (See Table 1 at in Ref. 2) without any optimization since the purpose of this work is not to add another fitting exercise in the parameter optimization choice.

The method of calculation to transform ab initio total electronic energy for a given compound into its enthalpy of formation can be illustrated through the following example. To calculate the heat of formation of ethyl radical at the 6-31G* basis set level, the sum of the atomic equivalents for the five H(C) (-0.56967 a.u.) plus C. (-37.90364 a.u.) and C-(C.) (-37.88712 a.u.) atoms (Table-1) is subtracted from the total energy of the ethyl radical (-78.59715 a.u.). And finally the multiplication by 627.52 kcal/mol x a.u. gives the estimated result (26.3 kcal/mol) for the heat of formation.

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