AN IMPROVED SIMPLIFIED SCHEME OF ATOM EQUIVALENTS TO RELATE AB INITIO ENERGIES TO ENTHALPIES OF FORMATION

Carolina Vericat and Eduardo A. Castro *

CEQUINOR, Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Calle 47 y 115, C.C. 962, 1900 La Plata, Argentina

E-Mail: castro@nahuel.biol.unlp.edu.ar
FAX: 54 - 21 - 259485

Abstract: An improved version of a previously simplified scheme of atom equivalents to relate ab initio total electronic energies to molecular enthalpies of formation (E. A. Castro, J. Mol. Struct. THEOCHEM **304** (1994) 93) is presented. The method is applied to the same sample molecules as in the previous paper and the new enthalpies of formation are in better agreement with the experimental data than former ones.

* Corresponding author

I-INTRODUCTION

The significant role that a knowledge of enthalpies (or heats of formation) of chemical systems plays in both basic and applied material sciences is well known /1/. The most important practical application of enthalpies ($\Delta H°_f$) is to explore reactivities and/or equilibria /2/. In many cases very accurate enthalpies of formation have been obtained experimentally. However, sometimes experimental data arising from different sources do not agree each other /3/ and experimental techniques are generally less successful for transient species, such as free radicals /4/.

On the other hand, an impressively large and rapidly increasing set of ab initio data for a wide variety of molecules gives the chemist the unprecedent opportunity to evaluate the energies of many species for which no experimental values are available /5,6/. Naturally, the chemist would like a simple way to relate these ab initio values to experimental energies. However, the existing procedures have some serious drawbacks such as the need to resort to experimental values for some components of the thermochemical cycle. These are not always available, hence,relatively few heats of formation have been estimated up to date from purely ab initio data /7/.

In order to surmount this sort of difficulty, some authors have published several methods of modeling $\Delta H°_f(g)$ and ab initio electronic energies at the equilibrium conformation with empirical parameters /7-15/. The justification for such a procedure has been discussed at length by Wiberg /8/ and by Dewar and Storch /16/. This approach is simple and remarkably accurate, often predicting heats of formation within 1-2 kcal/mol. In general terms, a satisfactory enough agreement was found between theoretical and experimental available data. The degree of theoretical accuracy is nearly the same as the experimental uncertainty, i.e. 1-2 kcal/mol.

In some previous articles of this series /15, 17-19/, one of the present authors (E. A. C.) has proposed a simplified scheme to relate ab initio energies to enthalpies of formation in gas phase and applied it to a large variety of molecules of molecules, radicals and ionic species. The concordance between theoretical values and experimental data was satisfactory.

The aim of this paper is to present an improved version of the precedent procedure and to apply it to a wide and significative set of molecules in order to show the usefulness of the method.

This article is organized as follows: in the next section we outline the method and the changes with respect to the previous scheme. Then we present the numerical results for a set of 62 sample molecules including acyclic and strained hydrocarbons, fluorinated and chlorinated hydrocarbons, and nitrogen and oxygen containing organic compounds. We make the corresponding comparisons with other theoretical results and available experimental data. Finally, we discuss the salient features of the present scheme and point out further possible applications of the method in order to calculate other molecular species and complementary physical chemistry properties.

II-METHOD

Ibrahim and Schleyer /7/ developed a set of atom equivalents which permitted the estimation of heats of formation $\Delta H°_f(g)$ from ab initio total electronic energies at the equilibrium geometries at the 3-21G and 6-31G* basis sets level. This procedure extended the isodesmic reaction scheme of Pople /2,20/ and the Wiberg's group equivalents /8/. However, in

order to take into account bonds of a given atom to different neighbours, Ibrahim and Schleyer assigned separate values to atoms in varied environments. In consequence, they resorted to a rather large class of atom equivalents. Later on, Yala /14/ simplified that approach via a linear-regression method to relate ab initio total electronic energies at the 6-31 G* basis set level to heats of formation. Instead of using the 56 parameters of the precedent scheme /7/, he only employed 11 parameters to study the same set of molecules. Since atomic eqivalents derived from the 3-21 G basis set do not yield satisfactory results for some compounds /7/, Yala /14/ restricted his scheme to the 6-31G* basis set level. Castro /15/ found that Yala's procedure to contract the original set of 56 parameters in Ref. 7 was rather arbitrary and leads to some contradictory results. Thus, he proposed to choose a simplified scheme on the basis of Ibrahim and Schleyer's parameters, characterizing each atom only by its coordination number and computing those data as average values from Table 1 in Ref. 7. Just one exception was made to this rule and it is related to the hydrogen atom, where he chose the same values as Ibrahim and Schleyer for the neutral species. The heats of formation derived from using such scheme of calculation showed a very good agreement with the available experimental data and a similar degree of accuracy to other similar theoretical procedures.

Notwithstanding, this way to choose atomic equivalents (although plainly democratic as it may be seem) is not totally well founded since in some cases an equal weight is given to quite different neighbours. For example, in order to define the carbon atom equivalent with coordination number 4, Castro proposed the -37.88685 a.u. (see Table 1 in Ref. 15) which arises from the arithmetic mean of the three equivalents given in /7/ (C-(H)$_3$C = -37.88937 a.u., C-(H)$_2$C$_2$ = -37.88750 a.u. and C-(H)-(C)$_3$ = -37.88371 a.u., Table 1 in Ref. 7). However, the set of molecules in these studies do not present many examples of ternary carbon atoms, and the greater number of molecules have primary and secondary C atoms, so it seems more reasonable to make the averaging between C-(H)$_3$-C and C-(H)$_2$(C)$_2$ equivalents, which gives the number -37.88843 a.u. A similar argument is applied to O and N atoms and it leads to a modified set of atom equivalents, which are shown in Table 1.

These atom equivalents yield the standard heat of formation through then direct and simple formula

$$\Delta H^{\circ}_f(g) = E_{el} - \Sigma_s k_s b_{is}$$

where E_{el} is the total molecular electronic energy at the equilibrium geometry, k_s is the number of atoms of each sort, b_{is} is the corresponding atom equivalent, and i denotes the coordination number of the s-th atom.

The transformation of the ab initio total electronic energy for a given compound into its enthalpy of formation can be clearly exemplified by the following example. To calculate the heat of formation of ethane, the sum of two single-bounded C atom equivalents (-37.88843 a.u.) and six H-(C) atom equivalents (-0.56967 a.u.) is substracted from the 6-31 G* total molecular energy (-72.22785 a.u.). The results is the enthalpy of formation (in hartrees), which must then be multiplied by 627.5 kcal/(mol x E_h) to give the value in kilocalories per mol: -20.69kcal/mol.

III-RESULTS

Tables 2-5 display the results for the same set of 62 sample molecules given in Refs. 7, 14 and 15, together with the experimental data and other theoretical values for comparison

purposes. Table 6 lists the Wiberg group equivalents /8/ and those derived from the C and H equivalents in Table 1 at the 6-31 G* basis set level.

The enthalpies of formation computed with the new set of atom equivalents via the scheme of calculation presented at the end of the last section show a satisfactory enough agreement with the available experimental values and a better degree of accuracy regarding the other theoretical procedures. The only noteworthy exception is the set of cyclohydrocarbons, where the average error is rather large, the same as it happens with some molecules such as glyoxal. Notwithstanding, these results are not unexpected at all since it is well known tha cyclic and polyciclic hydrocarbons must treated as a complete separate group requiring an additional set of parameters /10/ when one resorts to this kind of calculations. The main reason for this discrepancy arises from the fairly poor description of correlation energy at this level of ab initio calculation, so that a higher level of ab initio methodology should be necessary to have a better set of atom equivalents.

The analysis of group equivalents presented in Table 6 shows a reasonable agreement with other theoretical values, so that atom equivalents given in Table 1 could be suitable to define group equivalents in a calculation scheme for the estimation of heats of formation based on group additivities /2/.

IV-DISCUSSION

Since two centuries ago chemists have slowly, methodically and persistently transformed their way of talking about chemical compounds from a macroscopic viewpoint (formula, physical state, thermodynamical properties) to a structural one (atoms in molecules, functional groups, chemical bonds). With the astounding increase of the number of chemical compounds, chemical structures have become nearly the universal and valid language in discussing this huge number of chemical species. Accordingly, the present work has dealt with the decription of a traditional, macroscopic thermodynamical property, such as enthalpy of formation, via the language of molecular structure.

Although from a formal point of view it should be possible to calculate heats of formation from pure first principles methods, it is neither practical nor economical /21-25/. Thus, one is faced to employ some sort of theoretical method of an ab initio quality combined with a simple enough empirical procedure which yields a satisfactory estimation of the desired chemical and/or thermochemical property for a wide variety of molecular species.The method presented in Section II is based upon this inspiring guide and results displayed in Tables 2-6 have shown a remarkable accordance with available experimental data. Although the chosen molecular set is far from being complete and totally representative of the whole (and enormous) number of molecular possibilities, the agreement between theoretical results and thermochemical data should make it desirable to extend the application to other sort of molecules such as radicals, ions and inorganic species. Work along these lines is being carried in our laboratory and results will be presented elsewhere in the near future.

A final remark concerns the relationship between the model employed in the theoretical procedure (i.e. a single conformation of the molecule in the vibrationless state at 0 K) and the physical reality (i.e. experimental available enthalpies of formation are reported at 298 K and they refer to molecules existing at that temperature as a Boltzmann distribution of different isomers with somewhat different total electronic energies). Ab initio data can be corrected for these facts but it is known that these corrections do not change significantly the overall accuracy of the results derived from the scheme of atom equivalents /6/.

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TABLE 1. Atom equivalents

Atom	Coordination number	Notation	Value (a.u.)
C	4	C4	-37.88843
	3	C3	-37.88439
	2	C2	-37.88371
N	3	N3	-54.46869
	2	N2	-54.45619
	1	N1	-54.47074
O	2	O2	-74.79848
	1	O1	-74.79644
H-(C)	1	H_C	-0.56967
H-(N)	1	H_N	-0.56636
H-(O)	1	H_O	-0.56093
H-(F)	1	H_F	-0.56077
F	1	F	-99.34989
Cl	1	Cl	-459.46214

TABLE 2. Experimental and calculated heats of formation (kcal/mol) for acyclic hydrocarbons

Molecule	-E(6-31G*) a.u.	Experimental	This work	Castro /15/
Methane	40.19517	-17.89	-17.61	-18.60
Acetylene	76.81783	54.34	55.80	55.80
Ethylene	78.03172	12.45	9.88	9.88
Ethane	79.22785	-20.24	-20.69	-23.24
Propyne	115.86432	44.39	44.07	43.07
Allene	115.86110	45.63	43.97	45.94
Propene	117.07147	4.88	2.36	1.37
Propane	118.26365	-24.83	-25.73	-28.70
Dibutyne	152.49793	113.00	110.6	110.6
1,3-Butadiene	154.91960	26.11	22.58	22.58
2-Butyne	154.90925	34.71	33.29	31.31
1-Butene	156.10499	-0.20	-1.25	-3.23
(Z)-2-Butene	156.10786	-1.86	-3.05	-3.23
(E)-2-Butene	156.11041	-2.99	-4.65	-6.63
Isobutene	156.11067	-4.26	-4.81	-7.22
n-Butane	157.19841	-30.36	-30.11	-34.08
Isobutane	157.29896	-32.41	-30.46	-34.42
1,4-Pentadiene	193.94093	25.25	26.62	25.63

Average error: 0.65 this work
2.25 Ref. 15

Average absolute error: 1.47 this work
2.50 Ref. 15

TABLE 3. Experimental and calculated heats of formation (kcal/mol) for nitrogen andoxygen containing organic compounds

Molecule	-E(6-31 G*) a.u.	Experimental	This work	Castro /15/
Hydrogen cyanide	92.87520	32.30	30.70	28.62
Methyl amine	95.20983	-5.50	-6.89	-7.63
Methyl hydrazine	150.20108	22.60	20.59	20.11
Acetonitrile	131.92753	15.36	15.29	14.30
Acetaldimine	133.07384	2.00	0.13	0.90
Ethylamine	134.24761	-11.35	-13.17	-14.90
Dimethylamine	134.23885	-4.43	-5.60	-7.30
Cyanogen	184.59122	73.84	73.84	73.84
Formaldehyde	113.86633	-25.92	-28.96	-28.90
Methanol	115.03542	-48.07	-49.30	-50.48
Formic acid	188.76231	-90.57	-95.63	-95.81
Ketene	151.72467	-11.40	-13.05	-13.04
Acetaldehyde	152.91569	-39.73	-42.51	-43.67
Ethanol	154.07574	-56.24	-57.18	-55.94
Dimethylether	154.06574	-43.99	-45.42	-47.58
Glyoxal	226.59218	-40.66	-57.21	-57.21
Acetone	191.96225	-51.70	-54.30	-56.70
Formamine	168.93070	-44.50	-49.44	-49.19
Urea	223.98219	-58.70	-61.83	-61.33
Methylnitrite	243.66864	-15.60	-12.61	-14.88

Average error: 2.51 this work
                        3.00 Ref. 15

Average absolute error: 2.81 this work
                                    3.10 Ref. 15

TABLE 4. Experimental and calculated heats of formation (kcal/mol) for fluorinated and chlorinated hydrocarbons.

Molecule	-E(6-31 G*) a.u.	Experimental	This work	Castro /15/
Fluoromethane	139.03461	-55.9	-54.8	-55.9
Difluoromethane	237.89635	-107.0	-105.9	-106.9
Trifluoromethane	336.77164	-166.3	-165.6	-166.6
Fluoroethene	176.88195	-33.0	-34.0	-34.0
Fluoroethane	178.07722	-63.0	-64.1	-66.0
1,1-Difluoroethene	275.74000	-82.0	-82.9	-82.9
(e)-1,2-Difluoroethene	275.72173	-70.0	-71.4	-71.4
Tetrafluoroethene	473.41567	-157.9	-155.2	-155.2
trans-1,2-Dichloroethylene	995.83049	1.2	1.2	1.2
Vinylchloride	536.93369	8.6	3.9	3.9
1,1-Dichloroethane	997.03094	-30.7	-32.1	-34.1
(Z)-1,2-Difluoroethene	275.72130	-	-71.2	-71.1

Average error: 0.44 this work
              1.07 Ref. 15

Average absolute error: 1.46 this work
                      1.55 Ref. 15

TABLE 5. Experimental and calculated heats of formation (kcal/mol) of cyclohydrocarbons.

Molecule	-E(6-31 G*) a.u.	Experimental	This work	Castro /15/
Cyclobutane	156.09720	6.78	8.71	4.74
Cyclopentadiene	192.79192	31.94	32.69	31.70
Cyclopentene	193.97717	8.23	8.95	5.97
Cyclopentane	195.16295	-18.40	-15.12	-20.08
Cyclohexane	234.20796	-29.50	-25.94	-31.89
Cyclopropene	115.82305	66.20	70.81	69.81
Cyclopropane	117.05887	12.73	15.34	12.36
Cyclobutene	154.89962	37.45	40.18	38.20
Bicyclobutane	154.87169	51.90	57.71	55.73
Benzene	230.70305	19.81	13.37	13.37
Cubane	307.39383	148.70	170.08	149.75
Adamantane	388.02653	-32.51	-17.26	-27.18

Average error: 5.11 this work
               0.07 Ref.15

Average absolute error: 6.18 this work
                       2.50 Ref. 15

TABLE 6. Comparison of Wiberg group equivalents (a.u.)

Group	Wiberg	This work	Castro /15/
CH_3	-39.59842	-39.59744	-39.59586
CH_2	-39.02679	-39.02777	-39.02619
CH	-38.45274	-38.45810	-38.45652
$=CH_2$	-39.02541	-39.02373	-39.02373
$=CH$	-38.45321	-38.45406	-38.45406

Average absolute error: 0.000898 this work
0.001894 Ref. 15