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# 개선된 QSPR 방법에 의한 알켄의 생성열

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# Improved QSPR Prediction of Heats of Formation of Alkenes

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**요** 약. 탄화수소의 생성엔탈피를 예측하는 이전의 선형방정식들을 일반화하였다. QSPR 분석에서 사용된 분자를 표현하는 기본적인 인자는 원자와 화학결합이다. 이러한 선택은 이 방법을 매우 간단하게 하며 비용을 줄일 수 있게 한다. 19개의 알켄에 대한 예측치는 실험오차 정도의 편차를 준다. 이 방법의 몇몇 가능한 확장에 대해 지적하였다.

**ABSTRACT.** Some previous linear equations to predict hydrocarbon heats of formation are generalized. The basic molecular descriptors used for the QSPR analysis are atoms and chemcal bonds. This particular choice makes the method extremely simple and quite inexpensive. The predictions for a set of 19 alkenes yield deviations which are similar to experimental uncertainties. Some possible extensions of the method are pointed out.

## INTRODUCTION

The quite satisfactory results of applying Quantitative Structure Property Relationships (QSPR) to calculate heats of formation<sup>1-11</sup> seems to indicate this way is a suitable one to compute the enthalpy content of molecules. However, the usual numerical results do not represent true predicted quatities since the same set of molecules chosen to determine the fitting equations is employed to report the heats of formation. Since results are good enough and errors are nearly the same as experimental uncertainties, the QSPR equations show to be a suitable method to systematize data and to derive certain rules regarding the structural elements and group contributions to the molecular enthalpy of formation.

There are a wide variety of molecular descriptors to be used as independent variables in QSPR analysis and this large number of possibilities allows one to make quite different choices to perform the calculations and to interpret in a meaningful way the results. However, on spite of that, the most natural and directly available descriptors are not employed currently. In fact, the simplest way to describe topologically a molecule is to take into account the atoms and the classical chemical bonds. This particular election has led us to obtain quite satisfactory results in some previous QSPR studies<sup>3-6</sup> for several physical chemistry properties. Regarding hydrocarbon enthalpies of formation from *ab initio* calculations improved through bond parameters we have gotten very good correlations and predictions for a large enough set of hydrocarbons via linear relationships.<sup>3</sup>

Notwithstanding these significant features, one might hope to improve the extent of this sort of approximation by being able to make higher order calculations in order to arrive to more faithful correlations and predictions. Thus, we have deemed very interesting to perform such a sort of calculation in order to test the predictive capabilities of QSPR theory when employing this sort of "natural" molecular descriptors.

Accordingly, the aim of this paper is to report the heats

of formation of a set of representative hydrocarbons and a test set of alkenes on the basis of new second and third order polynomial regression equations, testing the results with the available experimental data and first order theoretical predictions.

The paper is organized as follows: next section deals with the basic equations and then we present the results for the chosen set, comparing the values obtained with other arising from different theoretical standpoints and discussing the relatives merits of each approximation. Finally, we state the main conclusions derived form this study and some possible further extensions.

#### METHOD

Five years ago, Herndon presented a simple enough protocol to convert Hartree-Fock *ab initio* total electronic energies for hydrocarbons to accurate heats of formation.<sup>12</sup> The optimum procedures use the number of carbon and hydrogen atoms ( $n_c$  and  $n_H$ , respectively) and 6-31 G\* nonrelativistic total electronic energies ( $E_{elect}$ ) as independent variables. Thus, the molecular enthalpy of formation at 298.15 K is given by

$$\Delta H^{o}_{f}(g) = A E_{elect} + B n_{C} + C n_{H} + D$$
(1)

where A, B, C and D are fitting parameters. The multilinear regression equations were calculated using the MATHEMATICA<sup>®</sup> standard software.<sup>13</sup>

Later on, the numerical relationships were improved through the determination of higher-order equations<sup>6</sup> and better agreements between experimental and theoretical data were obtained.

However, on spite of its quite satisfactory degree of accurace to predict molecular enthalpies of formation, the method was improved by means of the inclusion of the number and nature of chemical bonds. Consequently, it should take into account the existing differences among isomers, which under the previous approach they are considered equivalents.

According to Cioslowski,<sup>14</sup> a correction term must account for the electron correlation effects associated with bond formation and within this approximate scheme we have resorted to a more general equation than Eq. (1), *i.e.* 

$$\Delta H_{f}^{o}(g) = AE_{elect} + Bn_{C} + Cn_{H} + \sum_{i=j}^{bonds} b_{i-j}n_{i-j} + D \quad (2)$$

where  $n_{i,j}$  is the number of i-j chemical bonds and  $b_{i,j}$  is an empirical parameter obtained by multilinear regression analysis. The final linear fitting equations were<sup>3</sup>

$$\begin{split} \Delta H^{o}{}_{f}(g) &= 593.858373 \ E_{elect} + 22498 \ n_{C} + 338.850811 \ n_{H} \\ &- 0.620987 \ n_{C-C} - 1.181333 \ n_{C=C} \ 0.397152 \ n_{C=C} \\ &- 0.701003 \ n_{C-C(arom)} \end{split}$$

Standard Error = 1.4437, 
$$R^2$$
 = 0.9987, Average Deviation  
= 1.08  
 $\Delta H^o_f(g) = 589.899403 E_{text} + 22349.17 n_c + 336.410813 n_H$ 

$$\begin{array}{c} -0.626674 \ n_{\rm C-C} - 1.330811 \ n_{\rm C=C} \ 0.768674 \ n_{\rm C=C} \\ -0.787758 \ n_{\rm C-C(arom)} + \ 0.787197 \end{array} \tag{4}$$

Standard Error = 1.4504,  $R^2 = 0.9987$ , Average Deviation = 1.08

It is interesting to point out that regression equations can be interpreted as being mainly concerned with total electronic energy and the number of constituent atoms, with correction terms related to the different chemical bonds (i.e. compare coefficients A, B, C with  $b_{ij}$  ones).

We have concentrated in a rather specialized molecular set, which is the current approach for this sort of analysis, although this option does not necessarily implies a lack of molecular variations within such restricted choice. In fact, Herndon's choice of 65 hydrocarbons<sup>12</sup> comprises examples of planar, non-planar, alternant and non-alternant aromatic hydrocarbons, alkyl- and alkenylsubstituted benzene derivatives, acyclic and polycyclic alkanes, strained and unstrained olefines and alkynes. The fitting equations where then applied to a set of 19 selected alkenes<sup>15</sup> and quite satisfactory results were obtained.

But in order to take a step further to attain even better concordances between experimental and theoretical values, we have resorted to the determination of second and third-order fitting equations within the realm of the present approximation scheme. Some previous studies have shown that one can arrive to more meaningful quantitative agreements when using higher-order polynomial equations.<sup>4,6</sup> Then, final equations to correlate and predict molecular enthalpies of formation have the general form

$$\begin{split} \Delta H^{\circ}_{f}(g) &= A E_{elect} + A' E^{2}_{elect} + B n_{C} + B' n^{2}_{C} + C n_{H} + C' n^{2}_{H} \\ &+ \sum_{i-j}^{bond} b_{i,j} n_{i,j} + b'_{i,j} n^{2}_{i,j}] + D \end{split}$$
 (5)

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where A, A', A", B, B', B", C, C', C", b<sub>ij</sub>, b'<sub>ij</sub>, b"<sub>ij</sub> and D are empirical parameters determined with the aid of the set comprising 65 hydrocarbons (*i.e.* training set).

#### RESULTS

Here we present some representative results for the sake of conciseness, and complete data are available upon request to one of us (EAC). The second and third order multilinear regression equations are

$$\begin{split} \Delta H^{o}_{f}(g) &= 586.0365 \ E_{elect} - 0.0003 E^{2}_{elect} \ 22201.9580 \ n_{C} \\ &- 0.4468 \ n_{C}^{2} + 335.5647 \ n_{H} - 0.0745 \ n_{H}^{2} - 0.5169 \ n_{C(prim)} \\ &+ 0.0247 \ n_{C(prim)}^{2} - 0.0417 \ n_{C(sec)} - 0.2907 \ n_{C(sec)}^{2} \\ &+ 0.6105 \ n_{C(ter)} + 1.0098 \ n_{C(ter)}^{2} - 0.2511 \ n_{C(arom)} \\ &- 0.0108 \ n_{C(arom)}^{2} - 3.2420 \end{split}$$

$$\begin{split} \Delta H^o{}_{\rm f}(g) &= 581.1576 \,\, E_{\rm elect} - 0.0142 \,\, E^2_{\rm elect} + 0 \,\, E^3_{\rm \, elect} \\ &+ 22018.2954 \,\, n_{\rm C} - 21.1270 \,\, n^2_{\rm C} + 0.8187 \,\, n^3_{\rm C} \\ &+ 333.3537 \,\, n_{\rm H} - 0.3796 \,\, n^2_{\rm H} + 0.012 \,\, n^3_{\rm H} + 0.1135 \,\, n_{\rm C(prim)} \\ &- 0.0683 \,\, n^2_{\rm C(prim)} + 0.0082 \,\, n^3_{\rm C(prim)} + 0.1575 \,\, n_{\rm C(sec)} \\ &- 0.5062 \,\, n^2_{\rm C(sec)} + 0.1618 \,\, n^3_{\rm C(sec)} + 0.3806 \,\, n_{\rm C(tert)} \\ &+ 0.8042 \,\, n^2_{\rm C(tert)} + 0.7049 \,\, n^3_{\rm C(tert)} - 0.7150 \,\, n_{\rm C(arom)} \\ &+ 0.2452 \,\, n^2_{\rm C(arom)} - 0.0119 \,\, n^3_{\rm C(tarom)} - 5.6179 \end{split}$$

Experimental  $\Delta H^{\circ}_{f}(g)$  and the negative of calculated Hartree-Fock Self-Consistent Field (HF-SCF) electronic energies, optimized at the 6-31 G\* basis set level are listed in columns 3 and 2, respectively, in Table 1. The heats of formation modelled by first-, second-, and thirdorder polynomial equations are displayed in columns 4, 5, and 6, respectively. Predicted heats of formation of alkenes (test set) are given in Table 2.

We see that, in general, there is a quite satisfactory agreement betweeen theoretical and experimental results. Average deviations are even minor than experimental uncertainties (2-3 kcal/mol) and they diminish when the polynomial order increases. Furthermore, the true predictions (i.e. alkenes set) are very encouraging and practically there are not pathological cases. In this sense, present results makes up an improvement regarding former values derived on the basis of linear equations.

The largest deviation in the training set appears for the neopentane molecule (~ 4 kcal/mol). This fact is hardly surprising since the existence of two branches in neopentane with respect to the regular alkanes makes the variation of physical properties does not follow the normal pattern. In fact, it is well known the effect of branching on physical chemistry properties within all families of organic compounds. With branching, the shape of the molecule tends to approach that of a sphere and as this happens the surface area decreases, with the result that the intermolecular forces become weaker and are overcome with a minor energy expenditure.<sup>16</sup> Regarding the test set, only four molecules present somewhat large deviations when using the linear equation (3,3-dimethyl-1-butene; 2,3-dimethyl-2-butene; trans-1,2-di-t-butylethylene and trans-4,4-dimethyl-2-pentene), but all predictions fall within the same range of experimental uncertainties when resorting to second and third order formulae. Perhaps a more suitable way to organize calculations should be to consider branched molecules as a separate set and it would yield better numerical results. However, it should duplicate the number of fitting parameters. Since our main aim has been to provide a better alternative way to predict heats of formation instead of making numerical gymnastic, we have chosen the present way to make the calculations.

It is important to point out that present approximation is extremely simple and direct to apply (just to count atoms and chemical bonds !!) and these results reveals once again the significative relevance of the primary building blocks of the molecular structure.

#### CONCLUSIONS

We have verified the need to resort to higher-order polynomial equations when modeling molecular heats of formation. Certainly, whenever converting HF total molecular electronic energies to standard enthalpies of formation, it is convenient to employ higher-order multilinear regression equations in order to achieve chemical accuracy. In order to judge the relative merits of the present approximation scheme, we can compare the average absolute deviation obtained from a rather restricted molecular set (just four molecules) presented in Ref.<sup>15</sup> (1.81 kcal/mol) with present values (*i.e.* and for

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Table 1. SCF-HF total electronic energy (atomic units) calculated at the 6-31G\* basis set level and molecular enthalpies of formation (kcal/mol) for the training set.

| Molecule              | -Energy   | ALLOF(a) (and ) | $\Delta H^{\circ}f(g)$ | $\Delta H^{\circ}f(g)$ | $\Delta H^{\circ}(g)$ |
|-----------------------|-----------|-----------------|------------------------|------------------------|-----------------------|
|                       |           | ΔH I(g) (exp.)  | (linear equation)      | (quadratic equation)   | (cubic equation)      |
| Methane               | 40.19517  | -17.79          | -15.51                 | -15.98                 | -17.28                |
| Acethylene            | 76.81783  | 54.55           | 56.38                  | 55.18                  | 54.48                 |
| Ethylene              | 78.03172  | 12.56           | 12.58                  | 12.14                  | 12.03                 |
| Ethane                | 79.22876  | -20.04          | -20.04                 | -19.84                 | -20.36                |
| Propyne               | 115.86432 | 44.41           | 44.25                  | 44.40                  | 44.71                 |
| Allene                | 115.86110 | 45.31           | 44.88                  | 43.91                  | 44.22                 |
| Propene               | 117.07147 | 4.79            | 4.41                   | 4.74                   | 5.07                  |
| Propane               | 118.26365 | -24.93          | -25.96                 | -25.29                 | -25.30                |
| 1,3-butadiene         | 154.91965 | 26.01           | 25.62                  | 25.55                  | 26.19                 |
| 2-butyne              | 154.90926 | 34.69           | 33.02                  | 34.07                  | 34.46                 |
| 1-butene              | 156.10608 | 0.07            | -1.43                  | -0.57                  | -0.18                 |
| (Z)-2-butene          | 156.10786 | -1.77           | -1.77                  | -1.15                  | -1.01                 |
| (E)-2-butene          | 156.11041 | -2.84           | -3.28                  | -2.64                  | -2.49                 |
| Isobutene             | 156.11067 | -4.27           | -3.43                  | -2.79                  | -2.64                 |
| Cyclobutane           | 156.09720 | 6.78            | 4.59                   | 4.70                   | 5.20                  |
| n-butane              | 157.29840 | -30.33          | -30.55                 | -30.34                 | -30.69                |
| Isobutane             | 157.29897 | -32.24          | -30.88                 | -30.67                 | -31.02                |
| Cyclopentadiene       | 192.79172 | 32.12           | 32.83                  | 32.47                  | 32.81                 |
| 1,3-pentadiene        | 193.95916 | 18.29           | 17.60                  | 17.89                  | 18.08                 |
| 1,4-pentadiene        | 193.94721 | 25.27           | 24.65                  | 24.89                  | 24.98                 |
| Cyclopentene          | 193.97719 | 8.44            | 7.05                   | 7.50                   | 7.77                  |
| Cyclopentane          | 195.16358 | -18.26          | -19.28                 | -19.13                 | -18.84                |
| n-pentane             | 196.33302 | -35.60          | -35.68                 | -36.17                 | -36.40                |
| Cyclohexane           | 234.20800 | -29.49          | -30.20                 | -30.55                 | -30.44                |
| Cyclopropene          | 115.82305 | 66.22           | 67.40                  | 66.19                  | 66.47                 |
| Cyclopropane          | 117.05887 | 12.73           | 11.92                  | 11.62                  | 12.43                 |
| Cyclobutane           | 154.89961 | 37.45           | 37.52                  | 37.37                  | 37.89                 |
| Neopentane            | 196.33383 | -40.14          | -36.16                 | -36.64                 | -36.87                |
| Cubane                | 307.39391 | 148.69          | 146.41                 | 147.25                 | 147.54                |
| Bicyclo(1.1.0)butane  | 154.87177 | 51.90           | 54.03                  | 53.38                  | 54.09                 |
| Bicyclo(2.1.0)pentane | 193.92697 | 37.70           | 36.75                  | 36.72                  | 37.05                 |
| Bicyclo(2.2.0)hexane  | 232.96556 | 29.90           | 29.27                  | 29.33                  | 29.06                 |
| Bicyclo(2.2.1)heptane | 272.06116 | -12.40          | -11.84                 | -11.91                 | -12.00                |
| Bicyclo(2.2.2)octane  | 311.10358 | -23.67          | -21.58                 | -22.47                 | -22.21                |
| Spiropentane          | 193.91753 | 44.25           | 42.32                  | 42.25                  | 42.50                 |
| Bicyclo(2.1.0)pentene | 192.71022 | 79.70           | 80.98                  | 80.50                  | 80.02                 |
| Bicyclo(2.2.0)hexene  | 231.76849 | 62.50           | 61.90                  | 62.10                  | 61.10                 |
| n-hexane              | 235.36779 | -39.94          | -40.91                 | -42.55                 | -42.18                |
| Cycloheptatriene      | 269.68233 | 43.56           | 44.30                  | 43.59                  | 43.56                 |
| Norbornadiene         | 269.65251 | 59.18           | 61.97                  | 62.02                  | 60.16                 |
| Quadricyclane         | 269.61822 | 81.04           | 82.35                  | 82.87                  | 82.83                 |
| Cyclooctatetraene     | 307.52422 | 70.30           | 70.76                  | 70.85                  | 70.65                 |
| Benzene               | 230.70310 | 19.80           | 17.91                  | 17.90                  | 18.74                 |
| Naphtalene            | 383.35500 | 36.00           | 34.20                  | 34.54                  | 35.22                 |
| Anthracene            | 535.99880 | 55.20           | 55.27                  | 55.46                  | 55.45                 |
| Phenantrene           | 536.00980 | 49.70           | 48.78                  | 49.02                  | 49.09                 |

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| Molecule   | -Energy   | $\Delta H^{\circ}f(g)$ (exp.) | $\Delta H^{\circ}f(g) \qquad \Delta H^{\circ}f(g)$ |                      | $\Delta H^{\circ}(g)$ |  |
|--|-----------|-------------------------------|--|----------------------|-----------------------|--|
|  |           |                               | (linear equation)                                  | (quadratic equation) | (cubic equation)      |  |
| Bicyclo(2.1.0)pentane  | 193.92697 | 37.70                         | 36.75  | 36.72                | 37.05                 |  |
| Bez(a)anthracene   | 688.65688 | 68.10                         | 67.91  | 67.56                | 67.37                 |  |
| Chrysene   | 688.66090 | 66.00                         | 65.54  | 65.21                | 65.03                 |  |
| Triphenylene   | 688.66030 | 66.50                         | 65.89  | 65.56                | 65.38                 |  |
| Benz(c)phenanthrene  | 688.64950 | 69.60                         | 72.27  | 71.88                | 71.66                 |  |
| Pyrene   | 611.76800 | 54.00                         | 55.03  | 55.11                | 55.13                 |  |
| Perylene   | 764.40650 | 78.40                         | 79.23  | 78.63                | 78.89                 |  |
| Acenaphthene   | 460.26060 | 37.23                         | 36.43  | 37.04                | 37.07                 |  |
| Bhiphenylene   | 459.01460 | 99.80                         | 98.62  | 98.42                | 98.13                 |  |
| Acenaphthylene   | 459.07380 | 62.20                         | 63.70  | 63.75                | 63.96                 |  |
| Azulene  | 383.28260 | 73.53                         | 76.91  | 76.95                | 76.96                 |  |
| Fluoranthene   | 611.74562 | 69.20                         | 68.24  | 68.21                | 68.10                 |  |
| Cis-stilbene   | 537.13326 | 60.30                         | 59.44  | 59.81                | 60.45                 |  |
| Trans-stilbene   | 537.13943 | 56.40                         | 56.00  | 56.20                | 56.88                 |  |
| Biphenyl   | 460.25394 | 43.30                         | 41.30  | 41.51                | 41.78                 |  |
| o-xylene   | 308.77622 | 4.56                          | 5.35   | 5.70                 | 5.09                  |  |
| m-xylene   | 308.77724 | 4.14                          | 4.75   | 5.10                 | 4.50                  |  |
| p-xylene   | 308.77704 | 4.31                          | 4.87   | 5.21                 | 4.62                  |  |
| Styrene  | 307.58540 | 35.40                         | 34.29  | 34.99                | 33.35                 |  |
| Toluene  | 269.74016 | 11.95                         | 11.34  | 11.74                | 12.06                 |  |
| Average absolute error*  | -         | -                             | 1.08   | 0.97                 | 0.87                  |  |
| *Average absolute error= $\sum_{i=1}^{n}  \Delta H_{f}^{o}(g)(\exp)_{i} - \Delta H_{f}^{o}(g)(\text{theor.})_{i} /n$ ; n=number of molecules |           |                               |  |                      |                       |  |

#### Table 1. (continued)

| Table 2. Alkenes 6-31G* total electroni | e energies (atomic units) a | and enthalpies of formation | (kcal/mol) for the test set |
|---|-----------------------------|-----------------------------|-----------------------------|
|---|-----------------------------|-----------------------------|-----------------------------|

| Molecule                     | -Energy   | $\Delta H^{\circ}f(exp.)$ | $\Delta H^{\circ}f$ (lineal) | $\Delta H^{\circ}f$ (quadratic) | $\Delta H^{\circ} f$ (cubic) |
|------------------------------|-----------|---------------------------|------------------------------|---------------------------------|------------------------------|
| Cis-2-pentene                | 195.14229 | -6.60                     | -6.80                        | -7.17                           | -7.00                        |
| Trans-2-pentene              | 195.14504 | -7.62                     | -8.42                        | -8.78                           | -8.60                        |
| 2-methyl-2-butene            | 195.14577 | -9.99                     | -8.85                        | -9.21                           | - 9.48                       |
| 2-methyl-2-pentene           | 234.18020 | -15.99                    | -13.87                       | -15.23                          | -15.67                       |
| 2-methyl-1-butene            | 195.14370 | -8.44                     | -7.65                        | -8.02                           | -8.30                        |
| 3,3-dimethyl-1-butene        | 234.17395 | -14.46                    | -10.19                       | -11.57                          | -12.79                       |
| 3-methyl-1-butene            | 195.14116 | -6.60                     | -6.13                        | -6.50                           | -6.59                        |
| 2,3-dimethyl-2-butene        | 234.17701 | -16.30                    | -11.99                       | -13.36                          | -13.90                       |
| 2,3-dimethyl-1-butene        | 234.17700 | -14.96                    | -11.99                       | -13.35                          | -13.64                       |
| 1-mehtlcyclopentene          | 233.01793 | -0.91                     | -1.70                        | -2.40                           | -2.25                        |
| 3-methylcyclopentene         | 233.01300 | 1.77                      | 1.21                         | 0.48                            | 1.16                         |
| Cycloheptene                 | 272.04603 | -2.20                     | -2.99                        | -4.63                           | -3.50                        |
| 1-mehtylcyclohexene          | 272.05863 | -10.35                    | -10.42                       | -12.08                          | -11.57                       |
| Norbornene                   | 270.86184 | 21.51                     | 22.12                        | 21.11                           | 21.30                        |
| Cis-4,4-dimehtyl-2-pentene   | 273.20350 | -17.35                    | -12.33                       | -15.26                          | -16.27                       |
| Trans-4,4-dimethyl-2-pentene | 273.21254 | -21.22                    | -17.66                       | -20.55                          | -20.89                       |
| 2-bicyclo(2.2.2)octene       | 309.91244 | 4.90                      | 7.55                         | 5.80                            | 5.00                         |
| Cyclohexene                  | 233.01965 | -1.20                     | -2.71                        | -3.41                           | -2.78                        |
| Trans-1,2-di-t-butylethylene | 390.31453 | -39.56                    | -31.97                       | -42.49                          | -41.56                       |
| Average absolute error       | -         | -                         | 2.25                         | 1.44                            | 0.92                         |

second order and third order equations, respectively). Besides, the extreme simplicity of the method makes it very easy to apply, because it does not demand any sort of extra computational effort, and calculations are elementary and quite inexpensive.

Since this approximation has been employed just for one set of organic molecules, before stating more definitve conclusions about its relative qualifications, it should ne necessary to extend the procedure to different molecular sets (*i.e.* organic molecules including heteroatoms, inorganic compounds, radicals, ions, etc.). At present, work along this line is being carried out in our laboratory and results will be published elsewhere in the forthcoming future.

A final remark is in order to point out the existence of other important approximation schemes to predict heats of formation. Application of the group additivity method within the readily applicable version suggested by Benson et al.<sup>16-19</sup> has provided a powerful means of studying chemical on the basis of thermochemistry, alleviated planning of experimental estudies, evaluation of experimental results, estimation of the equilibrium and rate constants needed by simulation studies in olefin chemistry, oxidation, air pollution, etc. The transferable groups values relating to molecules are based on well-established experimental data on many compounds. At present we are analysing the application of similar equations as those employed in this work in order to extend this sort of approximation. Results will be given at due time elsewhere.

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