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Correlation between MO eigenvectors and enthalpies of formation for alkanes

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Abstract

A new model for the calculation of enthalpies of formation of alkanes (up to C_8) is presented. An additive bond energy scheme, using the experimental methane and diamond values for the C─H and C─C bond energies, respectively, is supplemented by correction for the C─C π antibonding character of the highest occupied molecular orbitals (HOMOs), effectively adjusting the C─C bond energies. The effect is calculated by the summation of products of appropriate eigenvectors from semiempirical PM3 or HF/STO-3G calculations, after orthogonal transformation. The enthalpy of formation can then be expressed in terms of only one adjustable parameter. With HF/STO-3G eigenvectors, the mean discrepancy between experimental and calculated enthalpies of formation, after a one-parameter correction for 1,4 steric interactions, is 2.2 kJ mol^{-1}, comparable with more highly parameterized models. The results using PM3 eigenvectors are less satisfactory, probably on account of the neglect of overlap in the semiempirical scheme.

Keywords: Alkanes; MO theory; Thermochemistry

1. Introduction

Calculations of the enthalpies of formation of gaseous substances cover a spectrum between highly parameterized empirical schemes and ab initio or density functional methods. Empirical schemes can be divided into two categories. First, there are additive group methods in which the standard enthalpy of formation $\Delta_f H^\circ$ is the sum of contributions from the groups that constitute the molecule; extensive tabulations of group values are given by Cohen and Benson [1] and Pedley et al. [2]. Alternatively, the experimental atomization enthalpy (obtained from the experimental enthalpies of formation of the substance and its constituent gaseous atoms) can be expressed in terms of one of several additive bond energy schemes. The simplest group and bond energy schemes can be shown to be equivalent, there being linear relationships among the parameters [3]. The various bond energy schemes differ basically in the ways in which the variability of bond energies from one molecule to another can be accommodated. Alkanes provide the simplest test of empirical methods. For example, in the Laidler scheme [3,4] the C─H bond energy E(C─H) for alkanes takes three values depending on whether the C atom is primary, secondary or tertiary. More recently, emphasis has been placed on variation of E(C─C), which can be related to the electronegativities of the groups connected by the C─C bond [5,6]. Another approach has been to recognize that the highest occupied molecular orbitals (HOMOs) in alkanes are C─C π antibonding [7–9]; this leads in effect to variations of E(C─C) that successfully explain the relative enthalpies of formation of isomers. These empirical methods – group and bond energy schemes – require up to four adjustable parameters for alkanes, although this can be reduced. For example, in the Allen bond energy scheme [10], as exploited with considerable success by Skinner [11,12], for unbranched alkanes only two adjustable parameters are needed if E(C─H)is fixed at the methane value (415.8 kJ mol^{-1}) and E(C─C) is then obtained from the experimental atomization enthalpy of ethane. In the Laidler scheme, E(C─C) can be fixed at the diamond value

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(357.4 kJ mol^{-1}), leaving three adjustable E(C–H) parameters; other empirical methods require values of E(C–C) that are up to 20 kJ mol^{-1} smaller than that found for diamond. Empirical schemes are considered to be satisfactory if they can reproduce experimental enthalpies of formation with an average discrepancy of around 2–3 kJ mol^{-1}, which is comparable with the experimental uncertainties for most small/medium organic molecules. Empirical corrections for steric effects have to be made where appropriate. Cao and Yuan [13] have developed a topologically based scheme, requiring five parameters for alkanes, with a novel treatment of steric effects, which we will mention later.

Molecular mechanics (MM) methods are competitive with these bond energy or group schemes. For example, the MM3 force field reproduces the experimental enthalpies of formation of alkanes at least as well as other empirical methods using two bond energy parameters plus increments for primary, secondary and tertiary carbon atoms [14].

At the other extreme ab initio Hartree-Fock (HF) and density functional (DFT) methods have become increasingly used since the 1980s when suitable programs became generally available. The 'raw' enthalpies of formation thus obtained invariably differ from experimental values by amounts far greater than the experimental errors, even with large basis sets and elaborate treatment of electron correlation. However, rational and systematic corrections can improve matters to the point that HF/DFT calculations may become competitive with empirical methods for small molecules at least [15]. For example, the enthalpies of formation of acyclic and cyclic alkanes having up to 12 carbon atoms can be reproduced with an average discrepancy of 1.5 kJ mol^{-1} by DFT/6–31G* calculations incorporating five adjustable parameters in expressions for bond and group equivalents (plus statistical mechanical corrections) [16,17]. Another approach to the conversion of HF or DFT energies into enthalpies of formation involves bond density functions to correct for electron correlation effects [18]. In the most recent work [19], linear regression corrections applied to the energies obtained from B3LYP/[6–311 + G(d, p)] calculations reduce mean errors in the enthalpies of formation of 180 small/medium organic molecules to about 10 kJ mol^{-1}; with analogous HF calculations the mean discrepancies are about 20 kJ mol^{-1}.

Popular semiempirical MO methods [20,21], such as MNDO, AM1 and PM3 are parameterized from a large database of experimental properties, but they fare poorly in calculating enthalpies of formation. For example, any successful modeling of alkane thermochemistry must lead to higher atomization enthalpies for branched chain molecules than for their straight chain isomers, as found experimentally, but the above semiempirical methods usually predict the reverse. Matters can be considerably improved by use of bond and group equivalents [22], analogous to the DFT calculations referred to above [16,17]. The PM3 and MNDO methods can also be improved by a pairwise distance directed Gaussian (PDDG) modification [23].

In this paper, we propose that a simple bond energy scheme for alkanes, using the methane value for E(C–H) and the diamond value for E(C–C), works well for alkanes if eigenvectors obtained from standard semiempirical and HF methods are incorporated. One of us has suggested [7–9] that the differences in energy among isomers in any homologous series can be attributed to the C–C π antibonding character of the HOMOs, which in effect causes variation of the C–C bond energy. Since antibonding MOs tend to be more destabilized than their bonding partners are stabilized relative to their constituent AOs, the occupancy of antibonding MOs has particularly important thermochemical consequences [7,24]. One way of quantifying the C–C antibondingness of an MO is by scrutiny of the products of eigenvectors of carbon 2p orbitals on adjacent atoms.

1.1. π Antibondingness $B^*(\pi)$

Consider the simple case of ethane, in its staggered conformation (D_{3d}). The HOMOs are a pair of degenerate orbitals of e_g symmetry [7]. Their antibonding character with respect to the C–C bond is apparent from the different signs of the eigenvectors c_1 and c_2 of the $2p_x$ and $2p_y$ orbitals on the respective atoms labeled 1 and 2, i.e.:

$$c_1(2p_x) = c_1(2p_y) = -c_2(2p_x) = -c_2(2p_y) \tag{1}$$

In Hückel theory [25], the π bond order B_{ab} between two bonded carbon atoms a and b is given by equation (2):

$$B_{ab} = \sum n_i a_i b_i \tag{2}$$

where a_i and b_i are, respectively, the carbon 2p AO coefficients for atoms a and b in the ith π MO and n_i is its occupation number (0, 1 or 2), the summation being performed over all π MOs. Thus, we can say that the occupancy of the e_g HOMOs in ethane weakens the C–C bond by an amount proportional to c^2, where $c = |c_1| = |c_2|$ in equation (1). More generally, we can write equation (3):

$$B_i(\pi) = c_{ij} c_{ik} \tag{3}$$

where $B_i(\pi)$ is a measure of the contribution made to π bondingness/antibondingness in the C_j–C_k bond by the ith filled MO, c_{ij} and c_{ik} being, respectively, the coefficients of carbon $2p_\pi$ atomic orbitals on adjacent atoms j and k. However, in the general case the 2p AOs whose coefficients are listed in the output from an MO calculation are not usually orthogonal to the bond axis, as in ethane. The appropriate orthogonal transformation of the local axes on each carbon atom results in both σ and π bondingness/antibondingness terms $B(\sigma)$ and $B(\pi)$. If the 2p AOs for each atom are abstract vectors in the same vector space as the atomic coordinates of the molecule, then the dot product of the vectors **U** and **V** of adjacent bonded atoms i and j in a molecule is given by equation (4):

$$\mathbf{U} \cdot \mathbf{V} = B(\pi) - B(\sigma) \tag{4}$$

The σ and π terms can be separated as follows. If the bond between atoms *i* and *j* is represented by an abstract vector **W**, then $B(\sigma)$ is the product of the projection of **U** and **V** along **W**. We can now write equation (5):

$$B^*(\sigma) = \mathbf{V} \cdot \mathbf{W}_{\text{unit}} \times \mathbf{U} \cdot \mathbf{W}_{\text{unit}} \tag{5}$$

where $\mathbf{W}_{\text{unit}}$ is a unit vector and a subspace of **W** and $B^*(\sigma)$ represents σ antibondingness, with $B^*(\sigma) = -B(\sigma)$. Thus, using equations (4) and (5) the quantities $B^*(\sigma)$ and $B^*(\pi)$ can be determined from the MO eigenvectors.

2. Results and discussion

Geometry-optimized MO calculations were performed using the semiempirical PM3 and ab initio STO-3G methods in the SPARTAN© package [26]. For those alkanes whose structural parameters have been collected by Montgomery [27], single-point calculations were also performed after geometry optimization using the MMFF94 force field [28]; except for 2,2,3,3-tetramethylbutane the results were not significantly different from those where geometry optimization was accomplished by MO calculations. The enthalpy of formation $\Delta_f H°(C_nH_{2n+2}, g)$ can be expressed as equation (6):

$$\begin{aligned}\Delta_f H^\circ(C_nH_{2n+2}, g) &= n[\Delta_f H^\circ(C, g)] + (2n+2)[\Delta_f H^\circ(H, g)] \\ &\quad - (n-1)E(C\text{–}C) - (2n+2)E(C\text{–}H) - k\sum B^*(\pi)\end{aligned} \tag{6}$$

where the summation in the last term is performed over all contiguous occupied MOs having overall C–C π antibonding character, i.e. positive values of $B^*(\pi)$. The enthalpies of formation of alkanes were taken from Pedley's compilation [29], while the JANAF tables [30] were consulted for $\Delta_f H°(C, g) = 716.67\ \text{kJ mol}^{-1}$ and $\Delta_f H°(H, g) = 218.00\ \text{kJ mol}^{-1}$. In equation (6), we have three unknowns: E(C–C), E(C–H) and k. In the first regression analysis, fitting only experimental data for molecules having no 1,4-*gauche* steric interactions and whose structures were geometrically restricted by the experimental values from Montgomery [27], E(C–H) was assigned the methane value of 415.87 kJ mol^{-1}. The HF/STO-3G calculations led to an E(C–C) value of 356.68 kJ mol^{-1}, remarkably close to the diamond value of 357.40 kJ mol^{-1}, with a small regression constant (intercept) of −0.62 kJ mol^{-1}. Accordingly, the regression was performed with E(C–C) constrained to the diamond value and with zero intercept; the constant k in equation (6) was found to be 60.0 and 84.0 kJ mol^{-1} for PM3 and HF/STO-3G calculations, respectively. In Table 1, experimental and calculated enthalpies of formation for alkanes are compared. Calculated values were sterically corrected (where appropriate) by allowing a constant 2.5 kJ mol^{-1} for each 1,4-*gauche* interaction, as recommended by Cox and Pilcher [3]. The agreement is significantly better with HF/STO-3G than with PM3. This may reflect the fact that the antibonding effect is better handled with a model that does not neglect orbital overlap, as in all NDDO based schemes of which PM3 is a member; the 'antibonding effect' on orbital energies is crucially dependent on overlap integrals [24]. The mean discrepancy between experimental and calculated (HF/STO-3G) values is 2.2 kJ mol^{-1}; in comparing this with the mean discrepancies of 1.7–3.0 kJ mol^{-1} obtained with variations of the four-parameter scheme [1,3] for the same data set it must be stressed that our model requires just one adjustable parameter, the constant *k*. The worst discrepancies share some common features; for example, 3,4-dimethylhexane and 3-ethyl-2-methylpentane both have a C_T–C_T bond (two 1,4-*gauche* interactions) adjacent to two C_S–C_T bonds, with one 1,4-*gauche* interaction each (S = secondary, T = tertiary and Q = quaternary). In 2,3,4-trimethylpentane, there are two adjacent C_T–C_T bonds. Standard empirical treatments [1,3] invoke additional correction terms for the 1,4 interactions across C_T–C_Q and C_Q–C_Q bonds of ca. 4 and 8 kJ mol^{-1}, respectively. Our HF/STO-3G calculations for 2,2,3-trimethylbutane give reasonably good agreement without any special treatment. However, there are serious discrepancies for 2,2,3-trimethylpentane and 2,3,3-trimethylpentane where the tertiary carbon atom is bonded both to a quaternary and to a secondary carbon. Thus, it appears that the simple additive approach to steric effects is inadequate where a tertiary carbon atom forming a C_T–C_T or C_T–C_Q bond forms additional sterically active bonds. Other authors have addressed this problem at the expense of further parameterization [11,31]. In the case of 2,2,4-trimethylpentane, a 1,5 steric interaction is doubtless responsible for the large discrepancy. Another poor result occurs with 2,3-dimethylhexane, with a discrepancy of 4.2 kJ mol^{-1}; this alkane has perplexed previous authors [2,11,32] and there is a suspicion that the quoted enthalpy of formation is in error

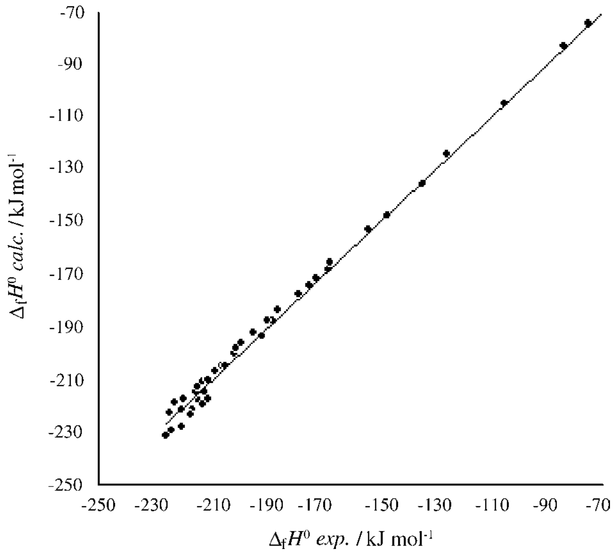

Fig. 1. Plot of calculated enthalpies of formation of alkanes against experimental values (kJ mol^{-1}).

Table 1
Experimental (exp) values of $\Delta_{\mathrm{f}}H^{\circ}$ for alkanes compared with values calculated from Eq. (6) (PM3 or HF), with residuals δ (all in $\mathrm{kJ\,mol^{-1}}$)

Molecule	$\Delta_{\mathrm{f}}H^{\circ}$ exp	$\Delta_{\mathrm{f}}H^{\circ}$[a] PM3	$\Delta_{\mathrm{f}}H^{\circ}$[a] HF	δ[b] PM3	δ[b] HF
Methane	−74.8	−74.8	−74.8	0.0	0.0
Ethane	−83.8	−84.0	−83.5	0.2	−0.3
Propane	−104.7	−104.7	−105.4	0.0	0.7
Butane	−125.7	−125.6	−124.8	−0.1	−0.9
2-Methylpropane	−134.2	−133.8	−135.4	−0.4	1.2
Pentane	−146.9	−149.1	−147.7	2.2	0.8
2-Methylbutane	−153.6	−153.3	−153.1	−0.3	−0.5
2,2-Dimethylpropane	−168.0	−164.2	−168.5	−3.8	0.5
Hexane	−166.9	−167.7	−165.7	0.8	−1.2
2-Methylpentane	−174.6	−175.0	−174.3	0.4	−0.3
3-Methylpentane	−171.9	−180.1	−171.6	8.2	−0.3
2,2-Dimethylbutane	−185.9	−184.9	−183.9	−1.0	−2.0
2,3-Dimethylbutane	−178.1	−180.6	−177.8	2.5	−0.3
Heptane	−187.6	−191.3	−187.5	3.7	−0.1
2-Methylhexane	−194.5	−194.6	−192.2	0.1	−2.3
3-Methylhexane	−191.3	−195.4	−193.3	4.1	2.0
3-Ethylpentane	−189.5	−191.9	−187.4	2.4	−2.1
2,2-Dimethylpentane	−205.7	−214.2	−204.7	8.5	−1.0
2,3-Dimethylpentane	−198.7	−198.7	−196.0	0.0	−2.7
2,4-Dimethylpentane	−201.6	−199.2	−200.3	−2.4	−1.3
3,3-Dimethylpentane	−201.0	−202.5	−198.4	1.5	−2.6
2,2,3-Trimethylbutane	−204.4	−208.3	−205.1	3.9	0.7
Octane	−208.5	−211.0	−207.1	2.5	−1.4
2-Methylheptane	−215.3	−217.5	−214.6	2.2	−0.7
3-Methylheptane	−212.5	−213.6	−210.9	1.1	−1.6
4-Methylheptane	−211.9	−217.1	−214.8	5.2	2.9
3-Ethylhexane	−210.7	−224.4	−209.8	13.7	−0.9
2,2-Dimethylhexane	−224.5	−225.0	−222.9	0.5	−1.6
2,3-Dimethylhexane	−213.8	−225.3	−218.0	11.5	4.2
2,4-Dimethylhexane	−219.2	−219.9	−217.6	0.7	−1.6
2,5-Dimethylhexane	−222.5	−220.8	−218.6	−1.7	−3.9
3,3-Dimethylhexane	−219.9	−223.0	−221.1	3.1	1.2
3,4-Dimethylhexane	−212.8	−220.3	−219.5	7.5	6.7
3-Ethyl-2-methylpentane	−211.0	−221.9	−217.7	10.9	6.7
3-Ethyl-3-methylpentane	−214.8	−226.1	−212.8	11.3	−2.0
2,2,3-Trimethylpentane	−219.9	−231.7	−228.3	11.8	8.4
2,2,4-Trimethylpentane	−223.9	−226.3	−229.4	2.4	5.5
2,3,3-Trimethylpentane	−216.2	−226.5	−221.4	10.3	5.2
2,3,4-Trimethylpentane	−217.2	−226.3	−223.2	9.1	6.0
2,2,3,3-Tetramethylbutane	−226.0	−252.6	−231.6	26.6	5.6

[a] Calculated enthalpies of formation.
[b] $\delta = \Delta_{\mathrm{f}}H^{\circ}$ exp. – $\Delta_{\mathrm{f}}H^{\circ}$ calc.

by some 3 $\mathrm{kJ\,mol^{-1}}$. Including all these anomalies, the mean discrepancy for the HF/STO-3G calculations is 2.2 $\mathrm{kJ\,mol^{-1}}$; this is comparable with the figure of 2.1 $\mathrm{kJ\,mol^{-1}}$ for the same molecules with the same prescription for steric corrections obtained with the ‘unified four-parameter scheme’ [3], but our method requires only the single adjustable parameter *k*. It will be apparent from the data in Table 1 that the discrepancies between experimental and calculated values increase rapidly with n for C_nH_{2n+2}. This is attributable to the increasing importance of steric effects with increasing *n*, and it is apparent that the simple counting of 1,4-*gauche* interactions is inadequate. The results are not significantly improved by adoption of the method of Cao and Yuan [13] for the treatment of steric effects, even at the expense of an additional adjustable parameter. We are presently investigating the use of MM methods to deal with steric effects. Further statistical analyses are collected in Table 2, while Fig. 1 shows a plot of calculated and experimental enthalpies of formation.

Table 2
Coefficient of determination (R^2) and sample standard deviation (s) between calculated and experimental enthalpies of formation for alkanes with and without corrections for steric interactions

	PM3	STO-3G
R^2	0.9698	0.9840
s	9.515	6.551
R^2[a]	0.9838	0.9942
s[a]	5.799	3.069

[a] Calculated after enthalpies were corrected for steric interactions.

3. Conclusions

The calculation of enthalpies of formation serves several purposes. There is a practical objective in developing reliable and inexpensive models where good experimental thermochemical data are lacking. Such calculations may also give insight into the reasons underlying such observations as the greater thermochemical stabilities of branched-chain alkanes compared with their straight-chain isomers and may provide at least semiquantitative support for qualitative arguments. The model adopted here, using HF/STO-3G rather than semiempirical PM3 eigenvectors, offers economy of both computational time and parameterization while giving results comparable in quality with more elaborate schemes. It also offers support for the proposition [7–9] that the C–C π antibonding character of the HOMOs in alkanes affects C–C bond energies in a way that reflects the relative stabilities of isomers. The model has scope for extension to substituted alkanes, helping to build bridges between largely empirical schemes [1–4,10–13,31,32] and rigorous but computationally expensive ab initio/DFT methods in which thermochemical subtleties (such as the relative stabilities of isomers) become submerged among thousands of integrals or are vaguely attributed to 'correlation energy effects'.

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