

ESTIMATING THE HEATS OF FORMATION OF HYDROCARBON RADICALS BY A SEMIEMPIRICAL CALCULATION

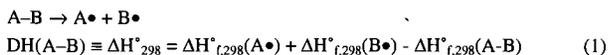
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INTRODUCTION

Hydrocarbon free radicals play a very important role in many thermal-chemistry processes, including combustion, petroleum and coal coking, coal liquefaction and pyrolysis, oil shale retorting, thermal stability of fuels as well as free radical polymerization. To obtain heats of formation (ΔH_f°) of the radicals is very essential for the fundamental understanding of thermal chemistry and mechanism of the free radical process. Many experimental methods have been developed to determine ΔH_f° of free radicals, including halogenation kinetics, polyani relation, chemical activation, equilibrium study, electron-impact measurement, radical buffer, appearance energy, photoacoustic calorimetry, electrochemistry etc.[1-3]. However, the experimental determination of ΔH_f° of free radicals is complicated, difficult and expensive due to the instability of the radicals. In consequence, many approaches have been developed to estimate ΔH_f° of the radicals.

Three principal methods have been developed to estimate ΔH_f° of free radicals. The first method, and also the best characterized, is Benson's group additivity method [4], which estimates the ΔH_f° by summing the contributions of the heats of formation of the various groups, and correcting for various higher order interactions via "correction" terms. The second method is the bond-dissociation-energy (BDE) method that was reviewed in detail by McMillen and Golden in 1982 [5]. BDE is defined as:



According to equation (1), $\Delta H_{f,298}^\circ(A\cdot)$ can be calculated if $DH(A-B)$, $\Delta H_{f,298}^\circ(A-B)$ and $\Delta H_{f,298}^\circ(B\cdot)$ are known. For the estimation of prototypical primary, secondary and tertiary alkyl radicals, McMillen and Golden recommended 98, 95 and 92 kcal/mol for $DH(\text{primary C-H})$, $DH(\text{secondary C-H})$ and $DH(\text{tertiary C-H})$, respectively. For allyl or aryl radicals, a correction term, "resonance stabilization energy" (RSE), was used.

Although both of these empirical estimation methods for hydrocarbon radicals are very common in the chemical literature, the accuracy of the methods is unsatisfactory. Recently, molecular orbital methods have been developed and used to calculate ΔH_f° of compounds, including neutral molecules, ions and radicals. There are two main molecular orbital methods, *ab initio* and semiempirical methods. Of these, the *ab initio* method, having no need for empirically determined parameters, is the more theoretically "pure". However, *ab initio* methods are currently slow, and routine application at any reasonable degree of accuracy to systems of larger molecule and to the calculation of a large number of molecules is still not practical. The semiempirical methods are fast enough for routine application to quite large systems, and to a large number of molecules. With the heats of formation of systems related to those for which the semiempirical methods were parameterized, the accuracy of semiempirical methods is comparable with that of quite large basis set *ab initio* calculations [6].

In 1989, Stewart developed the MNDO-PM3 method for further optimizing parameters of semiempirical methods [7,8]. Stewart calculated the ΔH_f° of 7 hydrocarbon radicals by using this method. The average difference between the calculated and experimental values is 6.24 kcal/mol. In 1996, Camaioni et al. calculated ΔH_f° of 19 hydrocarbon free radicals by the MNDO-PM3 method, and correlated the calculated values with the experimental values [9]. They found that the errors are systematic for families of structurally related radicals.

In this study, we attempt to develop a new method for estimating the ΔH_f° of the prototypical hydrocarbon free radicals. The new estimation method, called PM3-systematic-correlation (PM3-SC) method, is based on both the MNDO-PM3 calculation and correlation between the calculated values and the experimental values from the literature. The errors in Benson's, DBE and MNDO-PM3 and PM3-SC methods are also compared and discussed in detail via statistical analysis.

COMPUTATIONAL METHODS

All quantum chemistry calculations in this study were performed by means of the semiempirical MNDO-PM3 method [7,8], using CAChe MOPAC, version 94. Geometry of the radicals was optimized by using EF method, and the corresponding ΔH_f° of hydrocarbon free radicals were calculated by using doublet multiplicity.

SOURCES OF EXPERIMENTAL DATA

The experimental data are from the available literature. As the experimental data from different sources are somewhat inconsistent with each other, we made the widest possible use of currently common and accepted ones [1-3,5,9-12]. Some of ΔH_f° of alkyl radicals were determined by the empirical BDE method using new BDE parameters reported by Seakins et al.[3] (DH(primary C-H)=101.05, DH(secondary C-H)=98.26, DH(tertiary C-H)=96.44 kcal/mol).

RESULTS AND DISCUSSION

MNDO-PM3-calculated Results and Correlation with Experimental Data

The ΔH_f° values of 46 hydrocarbon free radicals, including primary alkyl, secondary alkyl, tertiary alkyl, alkenyl, aryl and cycloalkyl radicals, were calculated in this study by MNDO-PM3 method. Figure 1 plots the MNDO-PM3-calculated ΔH_f° vs. the experimental ΔH_f° for 46 hydrocarbon free radicals. As a whole, a considerable scatter exists with an R^2 value of 0.9535 and average errors of ± 10.57 kcal/mol. However, after examining the data, it is found that the structurally related radicals exhibit a very good linear correlation, as shown in Figure 1. According to the structural analogy of the radicals and the correlation, we can separate the 46 radicals into 5 groups. The first group consists of 15 primary alkyl radicals, including *n*-alkyl, *i*-alkyl, olefinic and phenylalkyl radicals with the experimental ΔH_f° values from 8 to 56 kcal/mol. A very good linear correlation between the experimental and calculated values was made by the least square fit with an R^2 value of 0.9982, although the calculated values are about 10 kcal/mol lower than the corresponding experimental values. The second group contains the secondary and tertiary radicals with an R^2 value of 0.9986. The MNDO-PM3-calculated values in this group are about 15-16 kcal/mol lower than the corresponding experimental values. The third group contains three cycloalkyl secondary radicals with an R^2 value of 0.9999. Alkenyl and aryl radicals together constitute the fourth group with an R^2 value of 0.9984, except for the 1-naphthylmethyl radical. The 1-naphthylmethyl radical deviates slightly from the regression line. Whether this deviation comes from the MNDO-PM3 calculation or from the experiment is still unclear. The last group consists of three cycloalkenyl radicals with an R^2 value of 0.9998.

The regression lines for alkyl radical groups, including the first, second and third groups, exhibit a similar slope, around 1.0, but with the corresponding intercepts different, being 11.71, 17.79 and 18.61 kcal/mol, respectively. The fourth group (alkenyl and aryl radicals), with intercept of 10.69 kcal/mol, shows the highest slope in all five groups, being 1.26. The group correlation reflects that the errors between MNDO-PM3-calculated and experimental values are systematic and dependent on the families of structurally related radicals. This finding allows one to be able to improve the accuracy of the estimates through scaling the calculated values. The linear regression equation for each group was obtained by a least squares fit. Using these regression parameters to scale the ΔH_f° calculated by the MNDO-PM3 method leads to a very significant reduction of the average error of the estimates, from ± 10.574 to ± 0.453 kcal/mol for the 45 hydrocarbon radicals.

Comparison of Different Estimation Methods Based on Statistical Analysis

In order to compare the errors from different estimation methods, the ΔH_f° values estimated by using Benson's, BDE and MNDO-PM3 methods, respectively, were also calculated. The calculation of ΔH_f° by Benson's method was performed according to reference [4]. The ΔH_f° values estimated by BDE method come from the review by McMillan and Coldren in 1982⁵. Statistical analysis of the errors for each methods was conducted. The experimental values vs. estimated values by Benson, BDE and MNDO-PM3 methods are plotted in Figure 2, 3 and 1, respectively.

With Benson's method, the expectation of errors is -2.901 kcal/mol, indicating the values estimated by this method are lower than the experimental values by about 3 kcal/mol as a whole. These errors can be attributed to that the experimental data used in specifying the group contribution to the ΔH_f° of the radicals in Benson's method are lower. For example, the experimental ΔH_f° values recommended in Benson's method were 26.5, 21.0, 17.6 and 8.4 kcal/mol for ethyl, *n*-propyl, *i*-propyl and *t*-butyl radicals, respectively, while recently, 28.9, 24.0,

21.5 and 12.2 kcal/mol were used instead [3]. The standard derivation of the errors in Benson's method is 1.909 kcal/mol, and thus, is scattered and unsatisfactory as Benson's method considers only the interaction between two linked atoms (short-range effect) and neglects the effect of interval atoms in the molecule (long-range effect).

The ΔH_f° values calculated by BDE method give an expectation of errors of -1.033 kcal/mol. It is still larger although being better than that for Benson's method. However, the standard derivation of the errors in this method is larger, being 2.497 kcal/mol. The errors in this empirical method are probably as the results of both using lower BDE values and using the BDE values derived from simple molecules to different and more complex molecules.

The ΔH_f° values estimated by MNDO-PM3 method exhibit larger errors. The expectation of errors is -8.108 kcal/mol, and the standard derivation is 8.908 kcal/mol, indicating that the ΔH_f° values calculated by the MNDO-PM3 method have to be scaled before use.

In all four methods discussed in this study, the PM3-SC method developed in this study gives the most accurate estimates, as shown in Figure 4. The expectation of errors is -0.001 kcal/mol, and the standard derivation is 0.575 kcal/mol. The statistical analysis indicates that we can use the PM3-SC method to estimate ΔH_f° of hydrocarbon radicals with a standard derivation below 0.60 kcal/mol. In other words, we can be 95 % confident that the difference between the estimated and experimental values is in the interval of ± 1.12 kcal/mol.

CONCLUSIONS

The families of structurally related radicals exhibit a very good linear correlation between the experimental and MNDO-PM3-calculated ΔH_f° values with the R^2 values higher than 0.998. On the basis of the MNDO-PM3 calculations, experimental data and statistical analysis, a new semi-empirical method, the PM3-SC method, has been developed to estimate ΔH_f° of hydrocarbon free radicals. The PM3-SC method can be used to estimate the ΔH_f° for almost all hydrocarbon radicals, including primary-alkyl, secondary-alkyl, tertiary-alkyl, alkenyl and aryl radicals. The PM3-SC method greatly improves the estimation accuracy and gives an average error of ± 0.453 kcal/mol only for the 46 hydrocarbon radicals, while the Benson's, BDE and MNDO-PM3 methods give the average error of ± 3.18 , ± 2.07 and ± 10.57 kcal/mol, respectively. The statistical analysis shows that with the PM3-SC method the difference between the experimental and estimated values is in the interval of ± 1.12 kcal/mol with 95 % confidence.

ACKNOWLEDGMENTS

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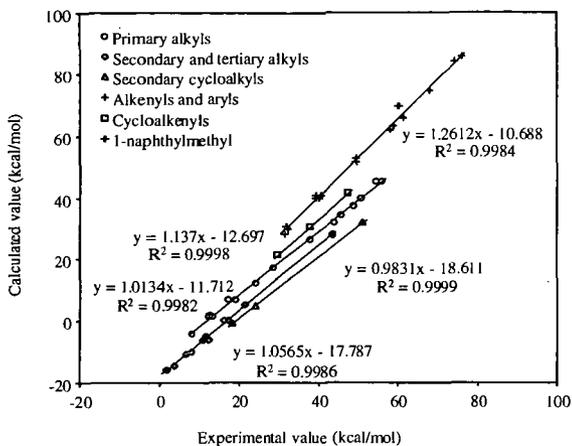


Figure 1 Correlation of MNDO-PM3-calculated ΔH_f° and experimental ΔH_f°

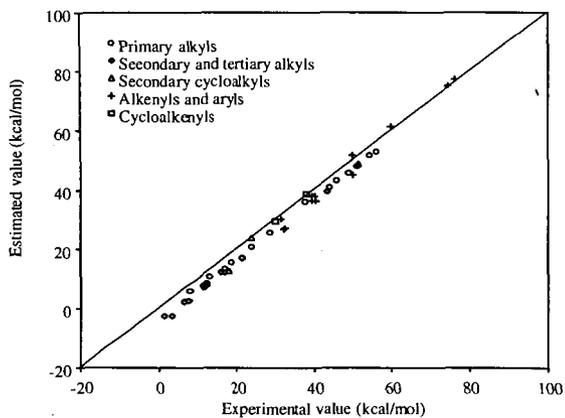


Figure 2 Benson-estimated ΔH_f° vs experimental ΔH_f° for hydrocarbon radicals

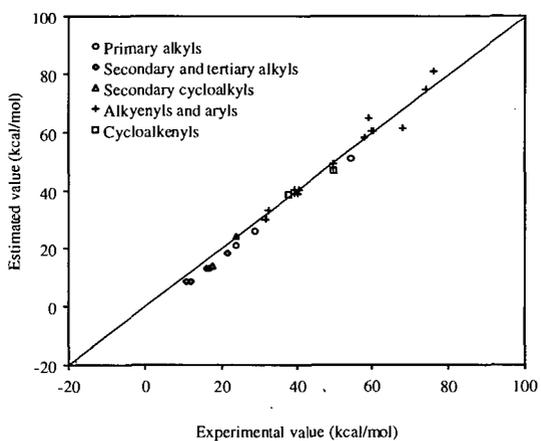


Figure 3 BDE-estimated ΔH°_f vs experimental ΔH°_f for hydrocarbon radicals

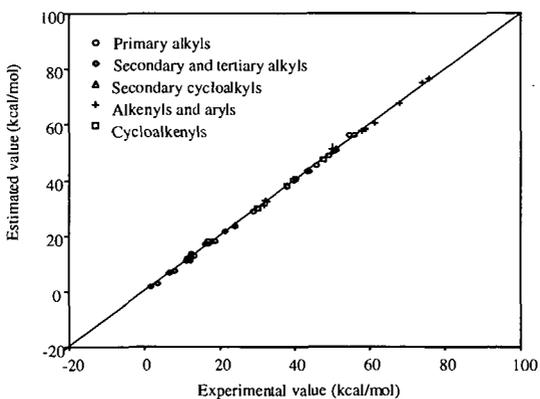


Figure 4 PM3-SC-estimated ΔH°_f vs experimental ΔH°_f for hydrocarbon radicals