Estimating Heats of Formation of Hydrocarbon Radicals by a Combination of Semiempirical Calculation and Family Correlation with Experimental Values

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A semiempirical method, the PM3-family-correlation (PM3-FC) method, has been developed to estimate the heats of formation ($\Delta H°_f$) of hydrocarbon free radicals. The PM3-FC method combines semiempirical PM3 calculations and family correlation with experimental data. The $\Delta H°_f$ values for a test set of 67 hydrocarbon free radicals, including alkyl, cycloalkyl, alken-α-ly, cycloalken-α-yl, arylalk-α-ly, alkyn-α-yl, and vinyl radicals, were calculated by using the PM3 method and then correlated systematically with the experimental values from the literature. According to the structural analogy of the radicals and the observed correlation, the 67 radicals in the test set can be separated into five groups. The MP3-calculated and experimental values of the radicals in each group exhibit a very good linear correlation. Using the obtained regression parameters to scale the PM3-calculated $\Delta H°_f$ values leads to a very significant increase in estimation accuracy. For the test set of radicals, excluding the three cyclic hydrocarbon radicals with three carbon atoms in the ring and the three methyl radicals coordinated with three unsaturated groups, the average absolute deviation and the standard deviation between the PM3-FC estimated and experimental enthalpy values are 0.8 and 1.1 kcal/mol, respectively. The 95% confidence limit of the deviation between the PM3-FC-estimated and experimental values is in the interval of ±2.1 kcal/mol. The error analysis of the PM3-FC method was preformed on the basis of statistical analysis by comparison with other estimation methods.

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, and free radical polymerization. To obtain standard-state heats of formation (or enthalpies of formation, $\Delta H°_f$) of the radicals is very essential for the fundamental understanding of the thermal chemistry and mechanism of the free radical processes. Many experimental methods have been developed to determine $\Delta H°_f$ of free radicals, including halogenation kinetics, the Polyani relation, chemical activation, equilibrium studies, electron-impact measurements, radical buffer, appearance energy, photoacoustic calorimetry, electrochemistry, gas-phase acidity cycles, photoionization, and mass spectrometry ion study.[1−4] Some excellent reviews of the $\Delta H°_f$ of organic free radicals from kinetic studies and from gas-phase ion studies have been given, respectively, by Tsang,[5] and Traeger and Kompe[6] in 1996. However, the experimental determination of $\Delta H°_f$ of free radicals is complicated, difficult, and expensive due to the instability of short-lived and highly reactive radicals. Thus, the experimentally determined $\Delta H°_f$ values of hydrocarbon radicals available in the literature are limited. In consequence, many approaches have been developed to estimate $\Delta H°_f$ of radicals on the basis of the empirical, semiempirical, or theoretical studies.

Francisco and Montgomery published a detailed review concerning the empirical, semiempirical, and theoretical studies of the energetics of radicals in 1996.[7] The best characterized method for estimating thermochemical properties of free radicals is the method developed by O'Neal and Benson[8,9] in accordance with the principles of group additivity propounded by Benson and co-workers,[10] which estimates the $\Delta H°_f$ by summing the contributions of the heats of formation of each group (group additivity values, GAVs), and correcting for various higher order interactions via "correction" terms. The group was defined as a polyvalent atom (ligancy ≥ 2) in a molecule together with all of its ligands. This group additivity method is based on the local nature of chemical forces. A set of 37 hydrocarbon GAVs and 16 hydrocarbon radical GAVs was evaluated by Benson and co-workers thirty years ago on the basis of the thermochemical data available at that time.[10] Since then, many GAVs have been revised in light of better experimental data. In 1989, based on new experimental data, Ni et al. tabulated a number of free radical GAVs,[11] including the GAVs for $\bullet C-(C_B)_2(H)$ and $\bullet C-(C_B)_2(C)$ groups, which were not given by Benson and co-workers in their earlier work.[10] In 1990, according to the analysis of GAVs involving the radical centered groups, Dilling derived another four new GAVs for hydrocarbon radicals, including $\bullet C-(C_d)_2(H)$, $\bullet C-(C_t)(H)_2$, $\bullet C-(C_t)(C)_2$, and $\bullet C-(C_t)(C)(H)$ groups.[12] In 1993, Cohen and Benson updated 37 hydrocarbon GAVs and seven hydrocarbon radical GAVs, and gave another 10 new hydrocarbon GAVs in light of new reliable experimental data.[13,14] The group additivity method has been the most popular and simple means of estimating unmeasured enthalpies of hydrocarbon radicals for thirty years. However, as mentioned by Cohen and Benson,[14] group additivity will become increasingly unreliable as molecular complexity, such as the number of neighboring functional groups, rings, or nonbonded interactions, increases. The nonbonded interaction and the large π-conjugation systems in large, complex radicals will probably be the ultimate limit of the accuracy of the group additivity

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method in predicting the enthalpies of radicals. Addition of correction terms in the procedure for nonneighboring effects (such as gauche, cis, rings, ortho, etc.) would increase the estimation accuracy, but also negate the comparative simplicity of the group additivity procedure.

Another method is using the bond-dissociation-energy (BDE) values experimentally determined from some simple molecules (or empirically or theoretically predicted) to calculate the unknown heats of formation of radicals, which was reviewed in detail by McMillen and Golden in 1982.[15] For the following reaction:

$$\mathrm{A{-}B} \rightarrow \mathrm{A}\bullet + \mathrm{B}\bullet$$

the BDE of A−B bond is defined as

$$\mathrm{DH(A{-}B)} \equiv \Delta H^{\circ}_{298} = \Delta H^{\circ}_{\mathrm{f},298}(\mathrm{A}\bullet) + \Delta H^{\circ}_{\mathrm{f},298}(\mathrm{B}\bullet) - \Delta H^{\circ}_{\mathrm{f},298}(\mathrm{A{-}B}) \quad (1)$$

According to eq 1, $\Delta H^{\circ}_{\mathrm{f},298}$ (A•) can be calculated if DH(A−B), $\Delta H^{\circ}_{\mathrm{f},298}$(A−B), and $\Delta H^{\circ}_{\mathrm{f},298}$(B•) are known. For the estimation of prototypical radicals, the DH(primary C−H) (or DH(secondary C−H) or DH(tertiary C−H)) value is assumed to be equal in different molecules. McMillen and Golden recommended 98, 95, and 92 kcal/mol for DH(primary C−H), DH(secondary C−H), and DH(tertiary C−H), respectively. For estimating the enthalpies of alken-α-yl or arylalk-α-yl radicals, a correction term, "resonance stabilization energy" (RSE), was used. In 1992, Seakins et al. recommended 101, 98, and 96 kcal/mol for DH(primary C−H), DH(secondary C−H), and DH(tertiary C−H) values, respectively, based on their new thermochemical data from kinetic studies.[16] Recently, Tsang recommended new BDE values for DH(primary C−H), DH(secondary C−H), and DH(tertiary C−H),[5] which are similar to the values recommended by Seakins et al.[16] The variety of the RSE values for different resonance systems in this estimating procedure hinders the extensive application of the BDE method in estimating enthalpies of complex radicals.

Although both of these estimation methods for hydrocarbon radicals are very common in the chemical literature, the accuracy of the methods is unsatisfactory, especially for the complex radicals, which will be further discussed in this paper. Recently, molecular orbital methods have been developed and used to calculate $\Delta H^{\circ}_{\mathrm{f}}$ of compounds, including neutral molecules, ions, and radicals. There are two main molecular orbital methods, ab initio and semiempirical molecular orbital methods. Of these, the ab initio method, having no need for empirically determined parameters, is the more theoretically "pure". Ab initio methods have been used to estimate the $\Delta H^{\circ}_{\mathrm{f}}$ of small species, and have been able to achieve an accuracy of 1−2 kcal/mol for the thermochemistry of small molecules.[17] Curtiss et al. reported well-established heats of formation at 298 K for a test set of 148 small species by Gaussian-2 (G2) theory and density functional theory (DFT).[18] By comparison of G2, G2(MP2), and G2(MP2, SVP) theories, they found that the G2(MP2, SVP) theory performs very well for hydrocarbons and radicals. For 22 small hydrocarbons and six small hydrocarbon radicals (the largest hydrocarbon radical in the set is the *tert*-butyl radical) in the test set, the average absolute deviations are 1.29 and 1.18 kcal/mol, respectively. With the DFT methods, they found that the B3LYP method performs the best in the seven different levels, being consistent with the findings by Bauschlicher.[19] With the B3LYP method, the average absolute deviations are 2.76 and 2.62 kcal/mol for the 22 hydrocarbons and the six hydrocarbon radicals, respectively. Another approach is the BAC-MP4 method (bond-additivity-corrected Møller−Plesset fourth-order perturbation theory method) developed by Melius and co-workers.[20−23] The BAC-MP4 method is based on their findings that the errors in the bond energies obtained from ab initio methods involving the correlated electronic wave functions are systematic and can be separated into errors due to individual bonds. This method is an ab initio calculation with empirical methods. They reported that the average difference between the BAC-MP4 estimated and experimental heats of formation was 1.3 for approximately ninety species. However, ab initio methods are currently still slow, and routine application at any reasonable degree of accuracy to the systems of larger molecules, especially to the calculation of a large set (from tens to hundreds) of species including larger radicals (containing more than 10 heavy atoms), is still impractical, if not impossible. To decrease the computational cost for producing accurate enthalpy estimates of the species by theoretical calculation, a computationally inexpensive theoretical prediction of molecular thermochemistry, which combines atomic equivalents, bond density functions and corrections for molecular charge and spin multiplicity, was presented by Cioslowski et al.[24] With this method at the B3LYP/6-311G** level, the average absolute deviation between the experimental and computed enthalpy values was 1.6 kcal/mol for a test set of 61 hydrocarbons, which contains six hydrocarbon radicals.

The semiempirical molecular orbital methods are fast enough for routine application to quite large molecular systems (the number of carbon atoms in the system can be higher than a hundred) and to a large set of molecules. With the heats of formation of systems related to those for which the semiempirical methods were parameterized, the accuracy of the semiempirical methods is comparable to that of quite large basis set ab initio calculations.[25] The semiempirical molecular orbital methods include MINDO/3,[26] MNDO,[27] AM1,[28] and PM3[29] methods. These methods determine both an optimum geometry and the electronic properties of molecules by solving the Schrödinger equation using the MINDO/3, MNDO, or AM1 semiempirical Hamiltonians developed by Dewar and co-workers,[26−28] or the PM3 semiempirical Hamiltonians developed by Stewart.[29] Dewar and co-workers compared the MINDO/3, MNDO, and AM1 methods and found that the average absolute derivations are 10.8, 6.3, and 5.5 kcal/mol, respectively, between the calculated and experimental $\Delta H^{\circ}_{\mathrm{f}}$ for a test set of 138 organic molecules.[28] For a set of six hydrocarbon radicals contained in the above test set, the average absolute derivations were found to be 9.5 and 5.6 kcal/mol by MNDO and AM1 methods, respectively. Stewart compared the MNDO, AM1, and PM3 methods and found that the average absolute deviations for a set of 657 compounds are, respectively, 13.9, 12.7, and 7.8 kcal/mol, indicating the PM3 method gives the best estimation accuracy in the three methods.[30] A great advantage of the semiempirical methods is their relative computational simplicity and low computational cost. An increase in the estimation accuracy by revising the parameters or by scaling the calculated values is necessary for the extensive application of the semiempirical calculation in estimating the $\Delta H^{\circ}_{\mathrm{f}}$.

In 1990, Camaioni calculated $\Delta H^{\circ}_{\mathrm{f}}$ values of 16 radicals (including 11 hydrocarbon radicals), 21 cations, and 33 radical cations by the AM1 method[31] and correlated the calculated values with experimental data. He found that for the cations and radical cations significantly better correlations are obtained if these species are divided into subclasses. In 1993, a group-corrected AM1 method was reported by Wang and Frenklach for estimating $\Delta H^{\circ}_{\mathrm{f}}$ of aromatics and aryl radicals,[32] which uses

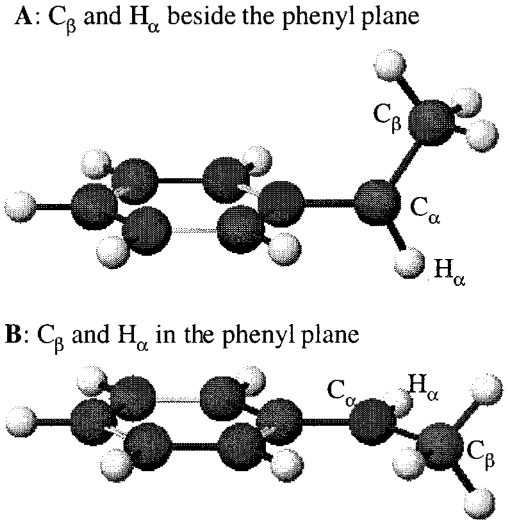

Figure 1. Two conformation of phenyleth-α-yl radical.

the group additivity correction values determined by known experimental data to scale the AM1-calculated values. In 1996, in the investigation of H transfer reactions by semiempirical molecular orbital methods, Camaioni et al. calculated $\Delta H°_f$ values of 19 hydrocarbon free radicals by the PM3 method.[33] After correlating the calculated values with the experimental values, they found that the deviations are systematic for families of structurally related radicals. The work of Camaioni et al. indicates that the PM3-calculated $\Delta H°_f$ values can be scaled by using the obtained correlation parameters to increase the estimation accuracy, provided that there are systematic and regular deviations for most hydrocarbon radical families and that their corresponding correlation parameters are obtained.

In this paper, we describe a method for estimating the $\Delta H°_f$ of hydrocarbon free radicals with an average absolute deviation between the calculated and experimental values within 1.0 kcal/mol. This estimation method combines the PM3 calculation and the family correlation between the calculated values and the experimental values. To facilitate discussion, this method is called as the PM3-family-correlation (PM3-FC) method. The error analysis of the PM3-FC method is conducted in comparison with other estimation methods on the basis of statistical analysis for a test set of 67 hydrocarbon radicals.

Computational Methods

All quantum chemistry calculations in this study were performed by means of the semiempirical PM3 method,[29] using the CAChe MOPAC program, version 94. Like other semiempirical methods, the PM3 method is based on a parameterized approximation to the Hartree−Fock self-consistent-field equations. Differing from others, the PM3 method uses 18 parameters for each element and 7 parameters for hydrogen, which were optimized on the basis of several hundred compounds.[29] In this study, geometries of the radicals were found by using the eigenvector following optimization (EF). The corresponding $\Delta H°_f$ of hydrocarbon free radicals were calculated by using doublet multiplicity.

For all arylalk-α-yl radicals examined in this study, the minimum-energy geometry located by the PM3 method shows that the C_β and H_α atoms (or two H_α atoms for benzyl radicals) are respectively beside the aryl plane, except 9-anthrylmethyl radicals. Figure 1a shows a conformation of phenyleth-α-yl radical corresponding to the minimum-energy geometry. The other conformation of the arylalk-α-yl radicals is one with both the C_β and H_α atoms (or two H_α atoms) in the aryl plane, as shown in Figure 1b for phenyleth-α-yl radical. This geometry gives a slightly higher calculated $\Delta H°_f$ value than that of the minimum-energy geometry by about 0.3−1.3 kcal/mol, depending on the specific structures of arylalk-α-yl radicals. However, many experiments have demonstrated that arylalk-α-yl radicals are more stable than alkyl radicals.[15] This stability is considered to be due to the resonance stabilization of an unpaired electron on the C_α atom with π-electrons on the aryl ring.[15,42] It indicates that the orbital of the unpaired electron (on the C_α) should be perpendicular, or approximately perpendicular, to the aryl plane. In other words, both the C_β and H_α atoms (or two H_α atoms) should be in (or close to) the aryl plane (see Figure 1b). As viewed from this point, we selected the $\Delta H°_f$ value corresponding to the conformation with the C_β and H_α atoms (or two H_α atoms) in (or close to) the aryl plane as the PM3 calculated values for all of the arylalk-α-yl radicals examined in this study.

Sources of Experimental Data

All experimental (or recommended) $\Delta H°_f$ values of hydrocarbon free radicals in this study are from the available literature. The appropriate citations to the sources of original data are given in Table 1. Assessment of the best current values for the radical enthalpies is beyond the scope of this paper, but readers can refer some excellent reviews.[4−6] As the experimental values from different sources are somewhat inconsistent with each other for some radicals, we made the widest possible use of currently common and accepted ones according to the recommended values from current and critical reviews or peer-reviewed papers. All of the experimental $\Delta H°_f$ values used in this study with their sources are listed in Table 1. For some values for which there is disagreement in the literature, we also list the different values from different sources for comparison.

Results and Discussion

1. PM3-Calculated Values and Global Correlation with Experimental Data. The $\Delta H°_f$ values of a test set of 67 hydrocarbon free radicals, including primary alkyl, secondary alkyl, tertiary alkyl, cycloalkyl, alken-α-yl, cycloalken-α-yl, arylalk-α-ly, alkyn-α-yl, and vinyl radicals, were calculated by the PM3 method. The results are listed in Table 1. Figure 2 plots the PM3-calculated $\Delta H°_f$ values vs the experimental $\Delta H°_f$ values of the radicals. As a whole, a considerable scatter exists, with an R^2 value of 0.9578 and an average absolute deviation between the PM3 calculated and experimental $\Delta H°_f$ values of 9.2 kcal/mol. The maximum deviation is −19.5 kcal/mol for cyclobutyl radical. A global correlation equation between the PM3 calculated and experimental $\Delta H°_f$ values for the set of radicals, excluding triethynylmethyl radical that deviates significantly from the regression line (see Figure 2), was obtained by the least-squares fit as below:

$$\Delta H°_{f,calc} = 1.2312\Delta H°_{f,exp} - 16.673 \quad (R^2 = 0.9615) \quad (2)$$

If using eq 2 to scale the PM3 calculated values, the average absolute deviation between the estimated and experimental $\Delta H°_f$ values for the test set, excluding triethynylmethyl radical, will decrease to 4.6 kcal/mol, and the maximum deviation is −11.9 kcal/mol for cyclobutyl radical. The average absolute deviation by this method (PM3-GC method), which combines the PM3 calculation and the global correlation with the experimental data, is close to those by the DFT calculations,[18] even comparable to those by some ab initio calculations for hydrocarbon radicals.[18]

TABLE 1: Comparison of Experimental and Estimated Heats of Formation for Hydrocarbon Radicals

			ΔH°_f (kcal/mol)		deviation (kcal/mol)				
no.	radical	structure	exp	PM3-FC	GA^c	PM3	PM3-GC	PM3-FC	ref
			Group 1						
	primary alkyl radicals								
1	ethyl	C−C•	28.9	28.8	−0.5	−11.6	−1.3	−0.1	4
			28.4						5, 34
			29.5						6
2	*n*-propyl	C−C−C•	23.9	23.6	−0.5	−11.9	−0.7	−0.3	5
			24.0						1
3	*n*-butyl	C−C−C−C•	18	18.2	0.4	−11.4	0.8	0.2	1
			18.7						33
			19.3						35
4	*n*-pentyl	C−C−C−C−C•	13	12.9	0.4	−11.9	1.4	−0.1	1
5	*n*-hexyl	C−(C)$_4$−C•	8	7.5	0.4	−12.3	2.0	−0.5	1
6	1-phenyl-eth-2-yl	Ph-C−C•	55.9	56.3	−0.5	−10.7	−5.7	0.3	36
7	1-phenyl-but-4-yl	Ph-C−C−C−C•	45.9	45.4	−0.5	−11.7	−4.6	−0.5	36
8	buten-4-yl	C═C−C−C•	49	48.7	−0.6	−11.5	−5.1	−0.3	33
9	penten-5-yl	C═C−C−C−C•	42.9	43.3	0.5	−10.9	−3.4	0.4	33
10	*n*-hexen-6-yl	C═C−C−C−C−C•	37.9	37.9	0.5	−11.3	−2.8	0.0	33
11	i-butyl	C−C(C)−C•	17.4	18.4	−1.4	−10.7	1.5	0.9	35
			16.7						5
12	cyclopropylmethyl	C−C−C−C•	51.5	56.2	2.2	−6.4	−1.4	4.7	15
	average absolute deviation				0.7	11.0	2.6	0.7	
	average absolute deviation,^{b} except no. 12				0.6	11.4	2.7	0.3	
			Group 2						
	secondary alkyl radicals								
13	i-propyl	C−C•−C	21.9	22.1	−0.9	−16.6	−4.2	0.2	6
			21.5						4, 5
			22.3						1
14	*sec*-butyl	C−C•−C−C	16.5	17.1	−0.5	−16.4	−3.0	0.6	5
			16.1						4
			17.0						1
15	*n*-pent-3-yl	C−C−C•−C−C	11.2	12.2	−0.2	−16.2	−1.8	1.0	33
16	*n*-pent-2-yl	C−C•−C−C−C	12	11.8	−1.0	−17.4	−2.9	−0.2	1
			11.2						33
17	*n*-hex-2-yl	C−C•−C−C−C−C	7	6.6	−1.0	−17.8	−2.3	−0.4	1
18	*n*-hept-2-yl	C−C•−C−(C)$_3$−C	2	1.7	−1.0	−17.9	−1.4	−0.3	1
19	1-phenyl-but-4-yl	Ph−C−C•−C−C	44.1	44.2	−1.1	−15.9	−7.7	0.1	36
20	1-phenyl-but-3-yl	Ph−C−C−C•−C	44.1	43.7	−1.1	−16.4	−8.1	−0.4	36
	tertiary alkyl radicals								
21	*tert*-butyl	(C)$_3$C•	11.5	11.1	−0.5	−17.6	−3.0	−0.4	5
			12.3						4
			12.4						35
			11.0						1
22	tert-pentyl	C−C−C•(C)$_2$	6.7	7.1	0.1	−17.0	−1.6	0.4	5
			7.8						37
23	3-methyl-3-pentyl	C−C−C•(C)−C−C	3.4	2.8	−1.6	−18.1	−1.9	−0.6	33
	average absolute deviation				0.8	17.0	3.4	0.4	
			Group 3						
	cycloalkyl radicals								
24	cyclpropyl	C−C•−C	66.9	77.9	−8.2	−8.9	−6.3	11.0	1, 15
			65						40
25	cyclobutyl	C−C−C•−C	51.2	51.2	1.6	−19.5	−11.9	0.0	15, 1, 34
26	cyclopentyl	C−C−C−C•−C	24	23.8	4.1	−19.2	−6.6	−0.2	1
			24.3						15, 34
27	cyclohexyl	C−C−C−C−C•−C	18	18.1	−1.3	−18.8	−5.2	0.1	1
	average absolute deviation				3.8	16.6	7.5	2.8	
	average absolute deviation,^{b} except no. 24				2.3	19.1	7.8	0.1	
			Group 4						
	alken-α-yl radicals								
28	allyl	C═C−C•	39.5	39.3	−1.5	0.1	6.2	−0.2	6
			39						1
			40.8						4
			40.9						5
29	1,3-pentadien-5-yl	C═C−C═C−C•	49.8	48.7	1.8	1.7	5.6	−1.1	33
			49						15, 34
30	1,3,5-heptatrien-7-yl	C═C−(C═C)$_2$−C•	60	59.5	5.1	5.1	6.3	−0.5	33
31	2-methyl-propen-3-yl	C═C(C)−C•	30.4	32.2	−0.3	0.7	8.4	1.8	15, 34
			29						1
32	1-buten-3-yl	C═C−C•−C	30.0	30.1	−0.1	−2.3	5.9	0.1	15, 34
			31.7						1
34	1-penten-3-yl	C═C−C•−C−C	25	26.3	0.3	−1.8	7.4	1.3	1
35	2-penten-4-yl	C−C═C−C•−C	22	21.3	0.6	−4.9	5.3	−0.7	1

TABLE 1 (Continued)

			ΔH°_f (kcal/mol)		deviation (kcal/mol)				
no.	radical	structure	exp	PM3-FC	GA^c	PM3	PM3-GC	PM3-FC	ref
			Group 4						
	alken-α-yl radicals								
36	trivinylmethyl	(CH$_2$=CH)$_3$C•	65.5	59.8		0.0	1.2	−5.7	40
37	cyclopentadienyl	C=C−C•−C=C	57.9	57.1	−2.2	4.1	6.0	−0.8	40, 34
			59						1
38	cycloheptatrienyl	C=C−C•−C=C−C=C	59	57.9	8.9	4.1	5.7	−1.1	1
			64.8						15, 40
	arylalk-α-yl radicals								
39	benzyl	Ph−C•	48.4	48.5	−0.7	2.8	6.7	0.1	4
			49						1
			49.5						5
40	1-phenyleth-1-yl	Ph−C•−C	39.6	40.0	0.0	1.0	6.8	0.4	1
			40.4						39, 15
41	1-phenyl-but-1-yl	Ph−C•−C−C−C	32.2	30.9	−2.6	−3.1	4.9	−1.3	36
42	2-phenylprop-2-yl	Ph−C•(C)$_2$	32.4	31.6	−5.0	−2.5	5.4	−0.8	1
			33.2						39, 15
43	1-phenylvin-1-yl	Ph−C•=C	74	74.9		10.5	8.1	0.9	40
44	diphenylmethyl	Ph−C•−Ph	67.9	66.9	1.0	6.6	6.1	−1.0	33
			69.0						40, 34
45	triphenylmethyl	(Ph)$_3$C•	92.5	88.2	−1.7	8.8	3.3	−4.3	40
46	9-anthrylmentyl		76	75.9	7.0	9.8	7.2	−0.1	33
47	9-phenanthrymethyl		74.3	74.6	6.3	9.8	7.6	0.3	33
			74.4						15
48	2-naphthylmethyl		60.2	62.9	5.2	9.2	9.7	2.7	33
49	1-naphthylmethyl		60.4	62.1	5.0	8.0	8.7	1.7	15, 34
			59.6						33
			60						1
50	9-hydroanthryl		61.4	59.9	1.7	4.2	5.4	−1.5	15
	average absolute deviation				2.9	4.6	6.3	1.3	
	average absolute deviation,^{b} except no. 36 and 45				2.9	4.6	6.7	0.9	
			Group 5						
	cycloalken-α-yl radicals								
51	cyclopropenyl	C=C−C•	105	104.7	−15.2	−2.8	−8.4	−0.3	15, 40
									1, 34
52	cyclopenten-3-yl	C=C−C•−C−C	38.4	39.1	0.2	−7.7	0.0	0.7	15, 34
			38						1
53	cyclohexen-3-yl	C=C−C•−C−C−C	30	30.6	−0.8	−8.7	0.8	0.6	10, 34
54	cyclohexadienyl	C=C−C•−C−C=C	49.7	48.8	6.5	−8.4	−2.7	−0.9	33
			47						15, 34
			50.0						41
	alkyn-α-yl radicals								
55	propargyl	C≡C−C•	81.0	81.7	1.5	−3.7	−4.7	0.7	5
			81.4						39, 15, 40, 34
			82						1
56	2-butyn-1-yl	C−C≡C−C•	70.2	72.1	2.5	−3.4	−2.4	1.9	15, 39, 34
57	2-pentyn-4-yl	C−C≡C−C•−C	65.2	61.5	−1.5	−10.1	−6.9	−3.7	15, 39, 34
58	4-methyl-2-pentyn-4-yl	C−C≡C−C•(C)$_2$	53.0	51.5	−0.7	−8.7	−3.5	−1.5	15, 39, 34
59	1-ethynyleth-1-yl	C≡C−C•−C	70.5	71.0	3.0	−4.9	−3.7	0.5	15, 39, 34
			73						1
60	2-ethynyl-i-propyl	C≡C−C•(C)$_2$	61.5	61.0	0.6	−6.9	−3.6	−0.5	15, 39, 34
			63						1
61	ethynylvinylmethyl	C≡C−C•−C=C	89	91.3	4.5	−1.2	−4.1	2.3	1
62	triethynylmethyl	(C≡C)$_3$C•	187.5	171.1	4.8	−12.4	−31.9	−16.4	40
	vinyl radicals								
63	vinyl	C=C•	71.5	69.1		−8.2	−6.6	−2.4	5
			71.6						4
			69.2						10
64	propen-2-yl	C=C•−C	55.3	57.1		−4.9	−0.9	1.8	40
65	1-cyclopropenyl	C=C•−C	124	141.7		19.0	5.5	17.7	40
66	1-phenylvin-2-yl	Ph−C=C•	92.5	90.9		−5.2	−8.1	−1.6	40
67	phenyl	Ph•	81.0	81.7		−3.7	−4.7	0.7	5
			78.9						4
			81.2						40, 34
	average absolute deviation				3.4	7.0	5.8	3.2	
	average absolute deviation,^{b} except no. 62 and 65				3.4	5.9	4.1	1.4	

TABLE 1 (Continued)

no.	radical	structure	ΔH°_f (kcal/mol) exp	ΔH°_f (kcal/mol) PM3-FC	deviation (kcal/mol) GA[c]	deviation (kcal/mol) PM3	deviation (kcal/mol) PM3-GC	deviation (kcal/mol) PM3-FC	ref
For Total Radicals									
average absolute deviation for the 67 radicals						9.18	5.07	1.62	
average absolute deviation for the 58 radicals[a]					2.20	9.36	4.63	0.97	
average absolute deviation[b]					2.09	9.17	4.75	0.79	
expectation of deviation[b]					0.46	−6.60	−0.07	0.00	
standard deviation[b]					3.39	8.54	5.42	1.09	
confidence interval (95%) of deviation[b]					−6.2, +7.1	−23.3, +10.2	−10.7, +10.6	−2.1, +2.1	

[a] The set excluded the nine radicals, the enthalpies of which fail to be estimated by the group additivity method, from the set. [b] The set excluded the three cyclic radicals with three carbon atoms in the ring and three methyl radicals coordinated with three unsaturated groups from the set. [c] The group additivity method.

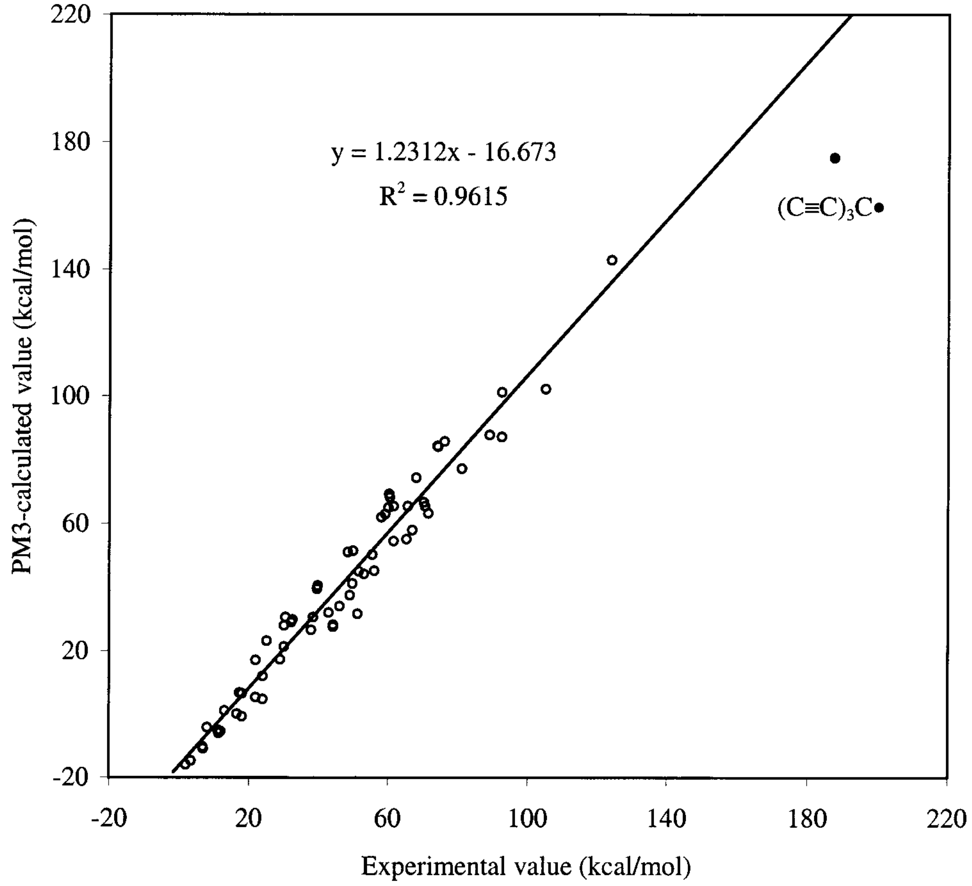

Figure 2. PM3-calculated ΔH°_f vs experimental ΔH°_f for hydrocarbon radicals.

However, for the practical application of estimating enthalpies of the radicals, such accuracy is still unsatisfactory.

2. Family Correlation with Experimental Data. On the basis of the structural homology of the radicals and the family correlation, we divide the 67 radicals into five groups and examine the correlation of each group separately.

Primary Alkyl Radicals. The first group consists of twelve primary alkyl radicals, including *n*-alkyl, *i*-alkyl, unresonant alkenylalkyl, and unresonant phenylalkyl radicals, with experimental ΔH°_f values from 8.0 to 55.9 kcal/mol. As shown in Figure 3, a very good linear correlation between the experimental and PM3-calculated values, except for the cyclopropylmethyl radical, was found, with an R^2 value of 0.9993. The calculated values for the primary alkyl radicals are about 11 kcal/mol lower than the corresponding experimental values. The linear regression equation obtained by the least-squares fit for the primary alkyl radicals, except cyclopropylmethyl radical, is given as below:

$$\Delta H^\circ_{f,calc} = 1.0149\Delta H^\circ_{f,exp} - 11.907 \quad (R^2 = 0.9993) \quad (3)$$

After using eq 3 to scale the PM3 calculated ΔH°_f values of the radicals, the average absolute deviation between the estimated and experimental ΔH°_f values decreases to 0.3 kcal/mol, which significantly increases the estimation accuracy. When applying eq 3 to the cyclopropylmethyl radical, a positive deviation of 4.7 kcal/mol was found. A possible reason for this deviation is that the experimental value of cyclopropylmethyl radical is from an early reference.[15] The earlier experimental values for the primary alkyl radicals have been found about 3 kcal/mol higher than the current values.[4,5] Another reason is a

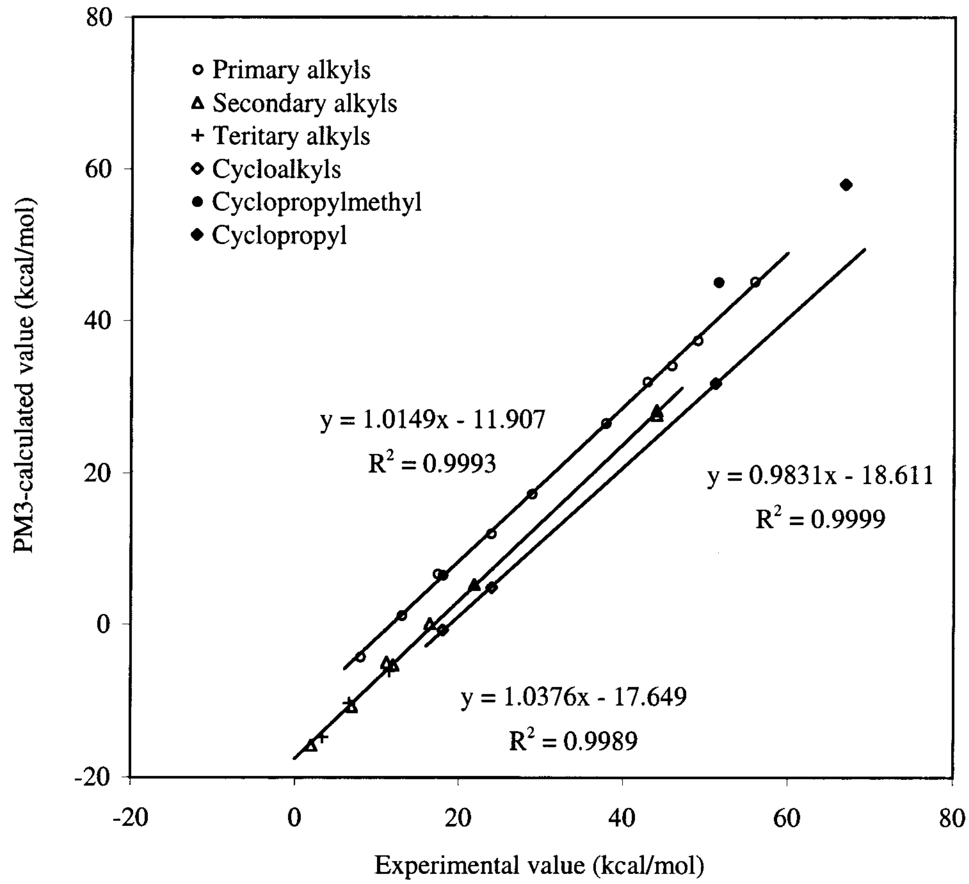

Figure 3. PM3-calculated ΔH°_{f} vs experimental ΔH°_{f} for alkyl and cycloalkyl radicals.

possible inherent PM3 calculation error that will be discussed later.

Secondary and Tertiary Alkyl Radicals. The second group consists of eight secondary and three tertiary alkyl radicals with the experimental ΔH°_{f} values from 2 to 44.1 kcal/mol. As shown in Figure 3, secondary and tertiary alkyl radicals exhibit a similar correlation between the experimental and PM3-calculated values with an R^2 value of 0.9989. The calculated values are about 17.0 kcal/mol lower than the corresponding experimental values. The linear regression equation obtained for the secondary and tertiary alkyl radicals is

$$\Delta H^{\circ}_{\mathrm{f,calc}} = 1.0376\Delta H^{\circ}_{\mathrm{f,exp}} - 17.649 \quad (R^2 = 0.9989) \quad (4)$$

Using eq 4 to correct the PM3-calculated ΔH°_{f} values of the secondary and tertiary radicals, the average absolute deviation decreases to 0.4 kcal/mol. The maximum deviation of +1.0 kcal/mol was found for the *n*-pent-3-yl radical.

Secondary Cycloalkyl Radicals. The third group contains four secondary cycloalkyl radicals with three to six carbon atoms in the ring and corresponding experimental ΔH°_{f} values from 18.0 to 66.9 kcal/mol. As shown in Figure 3, these radicals display a good linear correlation between the experimental and PM3 calculated values, except for cyclopropyl radical, which deviates significantly from the regression line. The linear regression equation obtained for secondary cycloalkyl radicals, except cyclopropyl radical, is given as follows:

$$\Delta H^{\circ}_{\mathrm{f,calc}} = 0.9831\Delta H^{\circ}_{\mathrm{f,exp}} - 18.611 \quad (5)$$

Using eq 5 to scale the PM3-calculated ΔH°_{f} values of cyclobutyl, cyclopentyl, and cyclohexyl radicals, the average absolute deviation is 0.1 kcal/mol. A positive deviation of 11.0 kcal/mol was found for the cyclopropyl radical if using eq 5 to scale the PM3-calculated ΔH°_{f} values. A possible reason for this large deviation will be discussed later.

Alken-α-yl and Arylalk-α-yl Radicals. Alken-α-yl and arylalk-α-yl radicals together constitute the fourth group, including eight alken-α-yl, two cycloalken-α-yl, seven phenylalk-α-yl, and five polycycloarylmethyl radicals with the experimental ΔH°_{f} values from 22 to 92.5 kcal/mol. All of the radicals in this group share the characteristic that the unpaired electron is in resonance with the π-electrons in unsaturated systems. These radicals display a similar correlation as shown in Figure 4. The 1-phenylvin-1-yl could be considered to be both a resonant radical and a vinyl radical. However, it provides a better correlation if we classify it into this group. Alken-α-yl and arylalk-α-yl radicals, except trivinylmethyl and triphenylmethyl radicals, give an excellent regression line with an R^2 value of 0.9956. The linear regression equation is given as below:

$$\Delta H^{\circ}_{\mathrm{f,calc}} = 1.2594\Delta H^{\circ}_{\mathrm{f,exp}} - 9.824 \quad (R^2 = 0.9956) \quad (6)$$

Using the obtained regression parameters in eq 6 to scale the PM3-calculated $\Delta \mathrm{H}^{\circ}_{f}$ values of the radicals, the average absolute deviation decreases to 0.9 kcal/mol. Trivinylmethyl and triphenylmethyl radicals deviate significantly from the regression line. The scaled values from eq 6 for trivinylmethyl and triphenylmethyl radicals are less than the experimental values by about 5 kcal/mol. This deviation will be further discussed later.

Cycloalkenyl, Alkyn-α-yl, and Vinyl Radicals. The last group consists of four cycloalkenyl, eight alkyn-α-yl, and five vinyl radicals, with experimental ΔH°_{f} values from 30 to 187.5 kcal/mol. In vinyl radicals, the unpaired electron is located at a sp^2 C atom, while in other radicals examined in this study the

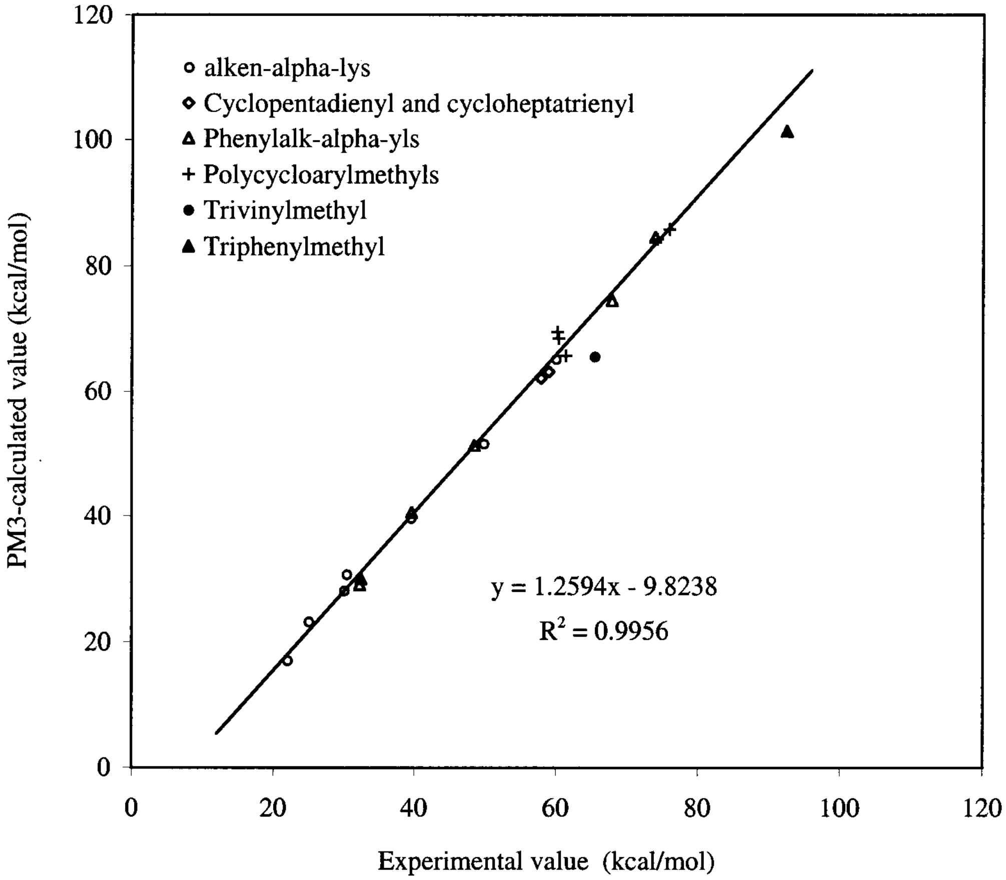

Figure 4. PM3-calculated ΔH°_{f} vs experimental ΔH°_{f} for alken-α-yl and arylalk-α-yl radicals.

unpaired electron is located at a sp^3 C atom. As shown in Figure 5, cycloalkenyl, alkyn-α-yl, and vinyl radicals, except the 1-cyclopropen-1-yl and triethynylmethyl radicals, show a linear correlation between the experimental and the PM3-calculated values, with an R^2 value of 0.993. Why these three kinds of the structurally different radicals display a similar correlation is unclear. The linear regression equation obtained by the least-squares fit is

$$\Delta H^{\circ}_{f,calc} = 1.0928\Delta H^{\circ}_{f,exp} - 12.165 \quad (R^2 = 0.993) \quad (7)$$

Using eq 7 to correct the PM3-calculated ΔH°_{f} values of the cycloalkenyl, propargyl, and vinyl radicals, the average absolute deviation between the estimated and experimental values for this group, except the 1-cyclopropen-1-yl and triethynylmethyl radicals, is 1.4 kcal/mol. When applying eq 7 to 1-cyclopropen1-1-yl and triethynylmethyl radicals, the deviations are very large, being +17.7 and −16.4 kcal/mol, respectively. The deviations for these two radicals will be discussed later.

The regression lines for alkyl radical groups, including the first, second, and third groups, exhibit a similar slope, around 1.0, but with different intercepts, being −11.907, −17.649, and −18.611 kcal/mol, respectively. The results show that there are significantly systematic deviations of the PM3-calculated ΔH°_{f} for alkyl radicals. The PM3 method underestimates ΔH°_{f} values of alkyl radicals. The negative deviations increase in the order of primary alkyl radicals, secondary and tertiary alkyl radicals, and secondary cycloalkyl radicals. The regression line for the fifth group has a slope of 1.0928, slightly higher than the values for the first three groups. The fourth group, containing alken-α-yl and arylalk-α-ly radicals, shows the highest slope, 1.2592, among the five groups. This slope indicates that the deviations of calculated ΔH°_{f} values in this group change with the ΔH°_{f} values. Of all the radicals in the test set, two kinds deviate significantly from the correlation lines in the PM3-FC method. One is the cyclohydrocarbon radicals with three carbon atoms in the ring, including cyclopropylmethyl, cyclopropyl, and cyclopropen-1-yl radicals. The other is the methyl radicals coordinated with three unsaturated groups, including trivinylmethyl, triphenylmethyl, and triethynylmethyl radicals. Interestingly, even for these exceptional radicals, the deviations of the PM3-calculated values from the correlation lines seem to be somewhat systematic. The three cyclohydrocarbon radicals have a positive deviation, as shown in Figures 3 and 5, while the three methyl radicals coordinated with three unsaturated groups have a negative deviation as shown in Figures 4 and 5. It is noted that the values for the three methyl radicals are from the same reference.[40] Whether these deviations result from an inherent PM3-calculation systematic error or from the experimental error is still unclear. More accurate experimental values for these kinds of the radicals may be necessary to determine the origin of deviations.

By examining the correlation of the PM3-calculated and experimental ΔH°_{f} values according to the structural homology of the radicals, we found that structurally related radicals exhibit a very good linear correlation. The excellent group correlativities suggest that the deviations between the PM3-calculated and experimental ΔH°_{f} values of the radicals are systematic and regular, depending on the families of structurally related radicals. This finding allows one to be able to improve the accuracy of the enthalpy estimates significantly by scaling the PM3-calculated values. Using the regression parameters obtained above to scale the PM3-calculated ΔH°_{f} leads to a very significant reduction of the average absolute deviation between

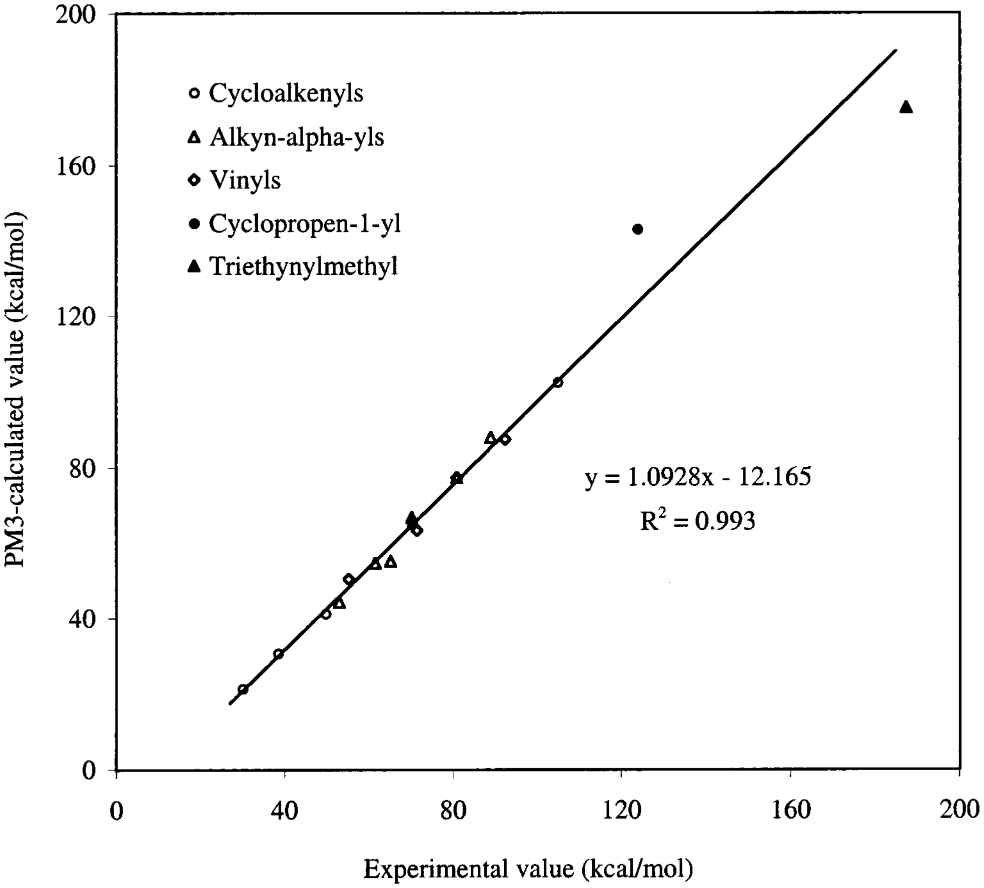

Figure 5. PM3-calculated $\Delta H°_f$ vs experimental $\Delta H°_f$ for cycloaken-α-yl, alkyn-α-yl and vinyl radicals.

the estimated and experimental $\Delta H°_f$. The experimental values vs the PM3-FC estimated values are plotted in Figure 6 for the test set of hydrocarbon radicals. An excellent agreement between the estimated and experimental enthalpies is observed, excluding the three cyclohydrocarbon radicals and the three methyl radicals.

3. Comparison of Different Estimation Methods on the Basis of Statistical Analysis. To compare the deviations from different estimation methods, the $\Delta H°_f$ values estimated by the group additivity, the PM3, and the PM3-GC methods were also calculated. The results are listed in Table 1. The group additivity method was performed by using the updated hydrocarbon and hydrocarbon radical GAVs[11,12,14] and correction values.[14] Statistical analysis of the deviations between the estimated and experimental enthalpies for each method was conducted.

For the unresonance-stabilized alkyl radicals, including primary, secondary, and tertiary alkyl radicals, the group additivity method performs well for estimating the $\Delta H°_f$ of the radicals, with an average absolute deviation of 0.8 kcal/mol for the 23 alkyl radicals in the test set. The PM3 and PM3-GC methods give average absolute deviation of 13.9 and 3.0 kcal/mol, respectively. The PM3-FC method shows the best accuracy of the four methods, with an average absolute deviation of 0.6 kcal/mol. If the cyclopropylmethyl radical is excluded from the set, the average absolute deviation will decrease to 0.4 kcal/mol.

For the cycloalkyl radicals, the average absolute deviation by using the group additivity method is 3.8 kcal/mol, much higher than that for the alkyl radicals using the same method. This indicates that the correction values that are applied to cyclo-compound enthalpy estimates in the group additivity method may not be suitable for the cyclic radicals. The average absolute deviation using the PM3 and the PM3-GC method is 16.6 and 7.5 kcal/mol, respectively. The PM3-FC method gives the least average absolute deviation, 2.8 kcal/mol for the cycloalkyl radical set and 0.1 kcal/mol for the set excluding the cyclopropyl radical.

For the resonance-stabilized radicals, in which the radical is stablized by the electronic delocalization over three or more carbon centers, including alken-α-yl, arylalk-α-yl, cycloalken-α-yl, and alkyn-α-yl radicals, the group additivity method gives an average absolute deviation of 2.9 kcal/mol, much higher than that for the unresonance-stabilized alkyl radicals by the same method. For the eleven polycycloarylmethyl and polyenylmethyl radicals in the set, the average absolute deviation is as high as 4.8 kcal/mol. This large deviation can be attributed to the fact that there is an “extra” stabilization in these kinds of polyenic and polycycloaromatic systems, and the group additivity method fails to take account of such “long-range” effects. The average absolute deviations by the PM3 and the PM3-GC methods for the same test set of the resonance-stabilized radicals are 4.6 and 6.3 kcal/mol, respectively. Among the four methods, the PM3-FC method performs best in estimating the enthalpies of such resonance-stabilized radicals, giving an average absolute deviation of 1.3 kcal/mol for this set of radicals. This is because the PM3-FC method takes account of various interactions via the PM3-calculation and corrects the deviations by the empirical parameters determined from experimental data. The PM3-FC method also performs well for the vinyl radicals, the average absolute deviation being 1.7 kcal/mol for the vinyl radical set, excluding cyclopropen-1-yl radical. The group additivity method cannot be used to calculate the enthalpy values for vinyl radicals and some resonance-stabilized radicals, because of the absence of the corresponding GAVs in the available literature.

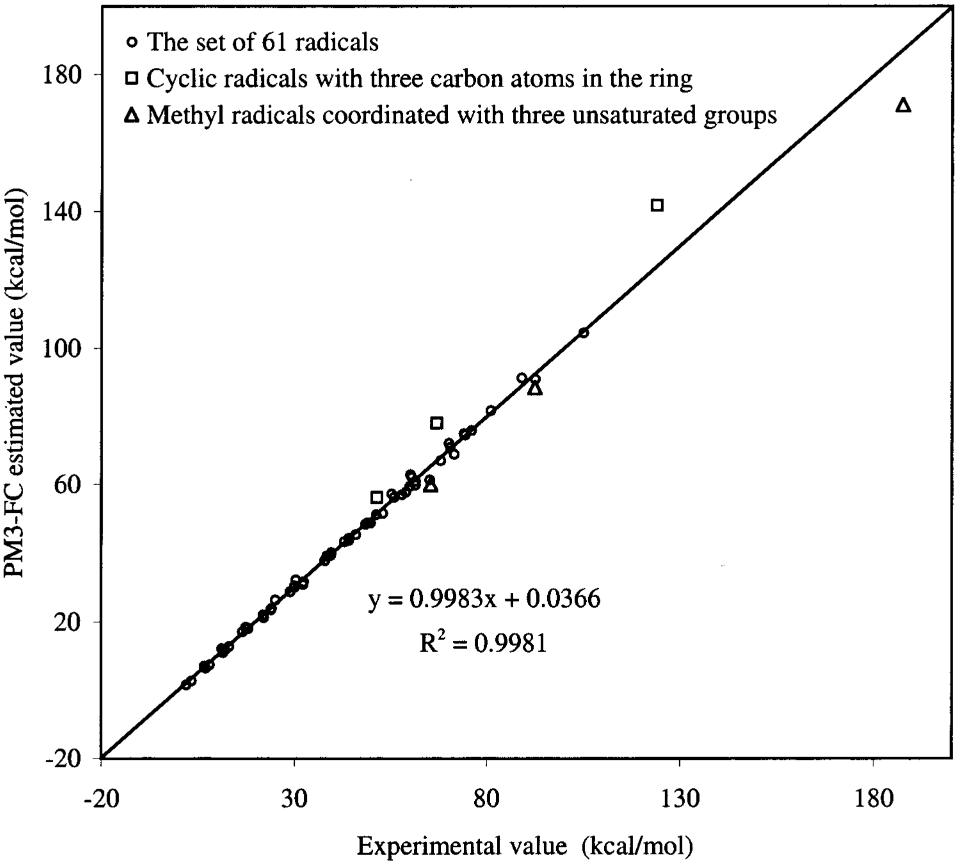

Figure 6. PM3-FC estimated ΔH°_f vs experimental ΔH°_f for hydrocarbon radicals.

As a whole, the group additivity method gives an average absolute deviation of 2.2 kcal/mol between the estimated and experimental enthalpy values for a set of 58 hydrocarbon radicals (the enthalpies of the other nine radicals in Table 1 cannot be estimated by the group additivity method due to the absence of the corresponding GAVs in the available literature). The PM3 method gives the largest average absolute deviation of the four methods, being 9.4 kcal/mol for the set of 58 hydrocarbon radicals. The PM3-GC method gives more accurate estimates than the PM3 method, the average absolute deviation being 4.6 kcal/mol for the same set. Hence, the PM3-GC method may be an acceptable alternative method when the estimated radicals do not belong to the groups classified in the PM3-FC method. Among the four methods discussed in this study, the PM3-FC method gives the most accurate estimates, with the average absolute deviation of 1.0 kcal/mol for the set of the 58 hydrocarbon radicals. For the whole set of 67 hydrocarbon radicals examined in this study, the PM3-FC method also performs very well, with the average absolute deviation of 1.6 kcal/mol. If the two kinds of the exceptional radicals (the three cyclohydrocarbon radicals and the three methyl radicals as discussed above) are excluded from the test set, the average absolute deviation and the standard derivation will be 0.8 and 1.1 kcal/mol, respectively. In other words, we can be 95% confident that the deviation between the PM3-FC-estimated and experimental values is in the interval of ±2.1 kcal/mol, which is comparable to most experimental errors in determination of the enthalpies of hydrocarbon radicals.[4-6]

It is worth pointing out that the PM3-FC method not only has a higher accuracy than the group additivity method and the ab initio calculation currently reported for estimating the hydrocarbon radical enthalpies, but it is also a convenient and computationally cheap method because the semiempirical PM3 calculation is relatively simple and of low computational cost. Only about thirty minutes on a Power Macintosh G3 computer is need to determine the geometry and to calculate the enthalpy of the largest radical listed in Table 1. We believe that the PM3-FC method is not limited to estimating the enthalpies of hydrocarbon radicals, but that such a method can also be used to estimate the enthalpies of other radicals, ions, intermediates, and transition state structures. Development of such a method will open up a bright future for the practical application of semiempirical molecular orbital calculations in estimating thermochemical properties.

Conclusions

A semiempirical method, the PM3-FC method, has been developed to estimate the heats of formation (ΔH°_f) of hydrocarbon free radicals. The PM3-FC method combines the semiempirical PM3 calculations and the family correlation with the experimental data. The ΔH°_f values for a test set of 67 hydrocarbon free radicals, including alkyl, cycloalkyl, alkenyl-α-ly, cycloalken-α-yl, arylalk-α-ly, alkyn-α-ly, and vinyl radicals, were calculated using the PM3 method, and correlated systematically with the experimental values from the literature. According to the structural homology of the radicals and the family correlation, we found that the radicals in the test set can be separated into five groups: primary alkyl radicals; secondary and tertiary alkyl radicals; secondary cycloalkyl radicals; alkenyl-α-ly and arylalk-α-ly radicals; and cycloalken-α-yl, alkyn-α-ly, and vinyl radicals. The MP3-calculated and experimental values of the radicals in each group exhibit an excellent linear correlation, with the R^2 values higher than 0.993, except for six particular radicals (the three cyclic hydrocarbon radicals with three carbon atoms in the ring and the three methyl radicals coordinated with three unsaturated groups). Using the obtained regression parameters to scale the PM3-calculated ΔH°_f values leads to a very significant improvement in the estimation accuracy. For a set of 61 hydrocarbon radicals, which excludes the three cyclic hydrocarbon radicals and the three methyl radicals, the average absolute deviation and the standard deviation between the estimated and experimental values is 0.8 and 1.1 kcal/mol, respectively. The PM3-FC method allows one to estimate accurately the heats of formation of most hydrocarbon radicals with 95% confidence that the deviation between the PM3-FC-estimated and experimental values is in the interval of ±2.1 kcal/mol. By comparison with other methods on the basis of statistical analysis, the PM3-FC method shows higher accuracy than the group additivity method and the current DFT and ab initio methods in estimating the heats of formation of hydrocarbon radicals, and is also a simple and computationally cheap method.

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