

Estimating the Activation Energy for Hydrogen Abstraction Reactions by a Combination of Semiempirical Calculation and Family Correlation

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A semiempirical method, the PM3-family-correlation (PM3-FC) method, has been developed to estimate the activation energies for hydrogen abstraction reactions between hydrocarbon radicals and hydrogen donors. The method combines semiempirical PM3 calculations of transition state enthalpies [$\Delta H_f^\ddagger(\text{TS})$] with family correlations between the PM3-calculated and experimental $\Delta H_f^\ddagger(\text{TS})$ values on the basis of regression analysis. For a test set of 40 hydrogen abstraction reactions, including alkyl + alkyl-H, alkyl + allylalkyl-H_α/arylalkyl-H_α, and benzyl + allylalkyl-H_α/arylalkyl-H_α, it is found that the deviations between the PM3-calculated and experimental $\Delta H_f^\ddagger(\text{TS})$ values are systematic and dependent on the transition state structures. The structurally homologous transition states show excellent linear correlation. Using the obtained linear regression parameters to scale the PM3-calculated $\Delta H_f^\ddagger(\text{TS})$ values leads to a very significant increase in estimation accuracy. The activation energies for the whole test set are estimated by using the scaled $\Delta H_f^\ddagger(\text{TS})$ values on the basis of the transition state theory. The average absolute deviation between the PM3-FC-estimated and experimental activation energies is 0.3 kcal/mol, with a standard deviation of 0.5 kcal/mol.

Introduction

Free-radical reactions play very important roles in a wide variety of thermal chemistry processes. One of the most important elementary reactions in free-radical processes is hydrogen abstraction, which involves hydrogen atom transfer from a hydrogen donor to a radical (a hydrogen acceptor).



Obtaining the activation energy (E_a) of hydrogen abstraction reactions is essential for a fundamental understanding of the hydrogen transfer mechanism and for the kinetic modeling of the processes. However, the experimental determination of the activation energy for hydrogen abstraction reactions is complicated and difficult, as most radicals are very unstable and short-lived. Thus, the experimentally determined E_a values available in the literature are limited. Consequently, many methods have been developed to estimate the E_a values for hydrogen abstraction reactions on the basis of empirical,^{1–14} semiempirical,^{15–22} or theoretical^{23–32} studies. Recently, the methods used in these studies have been reviewed by Marston et al.³³ and Denisov.³⁴

The Bell–Evans–Polanyi method^{1–3} can be expressed by eq 2, indicating that E_a is a simple linear function of the heat of reaction (ΔH_r).

$$E_a = \alpha \Delta H_r + E_0 \quad (2)$$

In this equation, α and E_0 are assumed to be constants

for a series of closely related atom-transfer reactions. E_0 corresponds to the value of the activation energy if the reaction were to occur with zero enthalpy. For the hydrogen abstraction reaction shown in eq 1, because $\Delta H_r = \text{BDE}(\text{R}'\text{-H}) - \text{BDE}(\text{R-H})$, eq 2 can be expressed by eq 3, where E_a is directly proportional to the R'-H bond dissociation energy [$\text{BDE}(\text{R}'\text{-H})$] of the hydrogen donor and α and β are assumed to be constants for a homologous series.

$$E_a = \alpha \text{BDE}(\text{R}'\text{-H}) + \beta \quad (3)$$

The structural contribution method reported by Willems and Froment¹² can be expressed by eq 4.

$$E_a = E_{\text{ref}} + \sum \Delta E_c \quad (4)$$

E_{ref} is the reference activation energy. ΔE_c is a correction term, depending on the structural contributions from the radical and the H donor. With this method, the average absolute deviation between the experimental and estimated E_a values was 1.2 kcal/mol for a test set of six hydrogen abstraction reactions.¹² The above three methods are the typical empirical methods, which involve neither the transition state enthalpy nor quantum chemical calculations.

Molecular orbital theory-based calculations have been used to examine the hydrogen abstraction reactions and to predict the corresponding E_a values. Most ab initio studies of hydrogen abstraction reactions focus on only one or a couple simple reactions, the transition states (TS) of which contain fewer than seven carbon atoms. The predicted E_a values from different investigators at different levels are also very distinct, making it difficult to draw meaningful conclusions about the statistical accuracy of the methods. Litwinowicz et al.²⁹ reported the estimation of E_a by using ab initio methods at

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different levels, including 3-21G, DZP, DZP* pVTZ, and pVTZ+. At the highest level (PMP4/pVTZ//HF/DZP*), the average absolute deviation from experimental E_a values was around 2 kcal/mol for a test set of six hydrogen abstraction reactions. The maximum deviation in the test set was 5 kcal/mol. The largest transition state structure in their test set contained only three carbon atoms. Because of the high computational cost, using ab initio methods at a high level to calculate a large set of TS structures including more than seven carbon atoms in the TSs is currently still impractical.

The major semiempirical molecular orbital methods include MINDO/3,³⁵ MNDO,³⁶ AM1,³⁷ and PM3.^{38,39} Based on a comparison of the MNDO, AM1, and PM3 methods for calculating enthalpies, Stewart reported that the average absolute deviations for a test set of 657 compounds are 13.9, 12.7, and 7.8 kcal/mol, respectively, indicating that, of these three semiempirical methods, the PM3 method gives the best estimation accuracy.³⁹ In 1996, Camaioni et al.²⁰ calculated the enthalpies of transition states [$\Delta H_f^\circ(\text{TS})$] for 22 hydrogen abstraction reactions by using the PM3 method. From a global correlation between experimental and calculated $\Delta H_f^\circ(\text{TS})$ values, they obtained a linear regression equation with an R^2 value of 0.9978.

$$\Delta H_{f,\text{calc}}^\circ(\text{TS}) = 1.143\Delta H_{f,\text{exp}}^\circ(\text{TS}) - 8.256 \text{ kcal/mol} \quad (5)$$

Using eq 5 to scale the PM3-calculated $\Delta H_f^\circ(\text{TS})$ values, the average absolute deviation was 1.2 kcal/mol for their test set, significantly decreasing the deviation compared to that of the PM3 method. A great advantage of the semiempirical methods is their relative computational simplicity and low computational cost. However, a further increase in the estimation accuracy by revising the calculation parameters or by calibrating the calculated values would be of great benefit for successful application of semiempirical calculations to estimations of the activation energy.

In our previous papers,^{40,41} we reported our approach to estimating the enthalpies of hydrocarbon radicals by a semiempirical calculation coupled with a family correlation with the experimental values. This work, and previous work reported by Camaioni et al.,²⁰ revealed that the deviations between the PM3-calculated and experimental enthalpies of hydrocarbon radicals are systematic for families of structurally related radicals. These findings suggested that the deviations between the PM3-calculated and experimental enthalpies for the transition states [$\Delta H_f^\circ(\text{TS})$] are probably systematic for families of structurally related transition states. Based on this idea, we attempted in the present study to estimate the $\Delta H_f^\circ(\text{TS})$ values for hydrogen abstraction reactions involving hydrocarbons by a method similar to that which we employed in estimating enthalpies of hydrocarbon radicals^{40,41} and, then, to compute the corresponding activation energies (E_a) from the estimated $\Delta H_f^\circ(\text{TS})$ values on the basis of transition state theory. The evaluation of the method presented here for estimating the E_a values was conducted by comparison with other estimation methods on the basis of deviation analysis for a test set of 40 hydrogen abstraction reactions involving hydrocarbons.

Computational Methods

All quantum chemistry calculations in this study were performed using a semiempirical molecular orbital

method, the PM3 method, in CAChe MOPAC, version 94. The PM3 method determines both the optimum geometry and the electronic properties of molecules by solving the Schrödinger equation using the PM3 semiempirical Hamiltonians developed by Stewart.³⁸ The geometries of the radicals involved in the hydrogen abstraction reactions were optimized by using the eigenvector following (EF) method, as reported in our previous paper.⁴¹ The transition state was defined by the reactants and products. The geometries of the transition states were located using the saddle calculation method followed by the Minimize Gradient method, and the corresponding $\Delta H_f^\circ(\text{TS})$ values were calculated using doublet option.

According to transition state theory,^{5,12,42–45} the Arrhenius activation energy E_a can be expressed by

$$E_a = \Delta H^\ddagger + (1 - \Delta\nu^\ddagger)RT \quad (6)$$

In this equation, $\Delta\nu^\ddagger$ is the change in number of moles in the transition from the reactant(s) to the activated complex. For bimolecular reactions, the value of $\Delta\nu^\ddagger$ is -1 . R and T are the ideal gas law constant and the temperature (K), respectively. ΔH^\ddagger is the standard activation enthalpy, which can be expressed by

$$\Delta H^\ddagger = \Delta H_f^\circ(\text{TS}) - \sum \Delta H_{f,\text{reactant}}^\circ \quad (7)$$

where $\Delta H_{f,\text{reactant}}^\circ$ is the enthalpy of the reactant. Thus, for the hydrogen abstraction reaction (eq 1), E_a can be expressed by eq 8, in which $\Delta H_f^\circ(\text{R}^\bullet)$ and $\Delta H_f^\circ(\text{R}'\text{--H})$ are the enthalpies of the radical and the hydrogen donor, respectively.

$$E_a = \Delta H_f^\circ(\text{TS}) - \Delta H_f^\circ(\text{R}^\bullet) - \Delta H_f^\circ(\text{R}'\text{--H}) + 2RT \quad (8)$$

Sources of Experimental Data

The experimental E_a values used in this study are from the available literature as identified in Table 1. The E_a values from different sources are somewhat inconsistent with each other for some reactions. Thus, we made the widest possible use of the self-consistent and currently recommended experimental data. For example, for the alkyl + alkyl-H reactions, we employed the E_a values recommended by the literature.^{46,47} For the reactions with a π -conjugated transition-state structure, we used the E_a values adopted currently by Camaioni et al.²⁰ The recommended values in the literature⁴⁶ were based on the average, weighted by considerations based on the criteria of Allara and Shaw.⁴⁶ In most cases, data that were totally inconsistent with an independent, consistent set of experimentally based values were rejected. Reassessment of the best experimental E_a values for these reactions is beyond the scope of the present paper. When the E_a values from the cited references are different from each other, an arithmetic mean was used. The experimental values of $\Delta H_f^\circ(\text{TS})$ were calculated from the experimental E_a values by eq 9, which is derived from eq 8.

$$\Delta H_{f,\text{exp}}^\circ(\text{TS}) = E_{a,\text{exp}} + \Delta H_{f,\text{exp}}^\circ(\text{R}^\bullet) + \Delta H_{f,\text{exp}}^\circ(\text{R}'\text{--H}) - 2RT \quad (9)$$

In eq 9, $E_{a,\text{exp}}$ is the experimental E_a value. The sources of experimental $\Delta H_f^\circ(\text{R}^\bullet)$ values are cited in our previous

Table 1. Estimated $\Delta H_f^\circ(\text{TS})$ Values and Activation Energies for H Abstraction Reactions (kcal/mol)

				$\Delta H_f^\circ(\text{TS})$			deviation of $\Delta H_f^\circ(\text{TS})$			activation energy			
no.	R'-H structure ^a	family	exp	PM3	PM3-GC	PM3-FC	PM3	PM3-GC	PM3-FC	PM3-FC		exp ^b	ref
										E_a	deviation		
by methyl radical: $\text{H}_3\text{C}^\bullet + \text{R}'-\text{H} \leftrightarrow \text{R}'^\bullet + \text{CH}_4$													
1	C	1st	30.6	28.5	32.7	32.6	-2.1	2.1	2.0	16.6	2.0	14.6	<i>c</i>
2	C-C	1st	25.2	21.1	26.4	25.5	-4.1	1.2	0.3	11.7	0.2	11.6	<i>c, d</i>
3	C-C-C	1st	20.3	15.5	21.6	20.1	-4.8	1.3	-0.2	11.3	-0.2	11.5	<i>d</i>
4	C-C-C-C	1st	15.0	10.0	16.9	14.8	-5.0	1.9	-0.2	11.2	-0.2	11.4	<i>c, d</i>
5	C-C-C-C-C	1st	9.7	4.6	12.3	9.7	-5.1	2.5	-0.1	10.8	-0.1	10.9	<i>e</i>
6	C-C-C-C	1st	18.8	14.1	20.4	18.7	-4.7	1.6	-0.1	9.9	-0.1	10.0	<i>c, d, e</i>
7	C-C-C-C-C	1st	13.6	9.2	16.2	14.0	-4.5	2.5	0.4	10.4	0.4	10.0	<i>c, d</i>
8	ph-C	3rd	55.3	55.4	55.7	55.4	0.0	0.3	0.1	9.6	0.1	9.5	<i>c, e</i>
9	C=C-C	3rd	47.4	46.7	48.2	47.4	-0.7	0.8	0.0	8.8	0.0	8.8	<i>d, e</i>
10	C ₃ C(t)-	1st	10.0	7.2	14.4	12.1	-2.9	4.4	2.0	10.3	2.0	8.3	<i>c, e</i>
11	ph-C(C) ₂	3rd	42.6	41.6	43.8	42.7	-1.1	1.2	0.1	7.9	0.1	7.8	<i>c</i>
12	C=C-C-C	3th	41.0	39.4	42.0	40.7	-1.6	1.0	-0.3	7.0	-0.3	7.3	<i>d, e</i>
13	C=C-C-C(C)-C	3th	34.6	33.0	36.5	34.8	-1.7	1.9	0.2	7.5	0.2	7.3	<i>c, d</i>
average absolute deviation							2.9	1.7	0.4		0.4		
average absolute deviation ⁱ							3.0	1.5	0.1		0.1		
by ethyl radical: $\text{CH}_3-\text{H}_2\text{C}^\bullet + \text{R}'-\text{H} \leftrightarrow \text{R}'^\bullet + \text{CH}_3-\text{CH}_3$													
14	C-C	2nd	21.0	12.7	19.1	21.0	-8.4	-1.9	0.0	13.4	0.0	13.4	<i>c, f</i>
15	C-C-C	2nd	15.0	6.1	13.5	14.9	-8.9	-1.5	-0.1	12.2	-0.1	12.3	<i>d</i>
16	C-C-C-C	2nd	9.8	0.5	8.8	9.8	-9.3	-1.1	0.0	12.3	0.0	12.3	<i>d</i>
17	C-C-C-C	2nd	14.1	4.9	12.5	13.8	-9.2	-1.6	-0.3	11.1	-0.3	11.4	<i>c, d</i>
18	C-C-C-C-C	2nd	7.9	-1.2	7.3	8.3	-9.1	-0.6	0.4	10.8	0.4	10.4	<i>d</i>
19	C ₃ C(t)-	2nd	5.6	-2.6	6.1	6.9	-8.3	0.4	1.3	11.3	1.3	10.0	<i>c</i>
20	ph-C	4th	49.7	45.6	47.3	49.5	-4.1	-2.4	-0.2	9.8	-0.2	10.0	<i>e, g</i>
21	C=C-C	4th	42.3	37.9	40.7	42.5	-4.4	-1.6	0.2	10.0	0.2	9.8	<i>d</i>
22	C=C-C-C	4th	35.9	30.5	34.4	35.9	-5.5	-1.5	-0.1	8.2	-0.1	8.3	<i>d</i>
average absolute deviation							7.5	1.4	0.3		0.3		
average absolute deviation ^j							7.4	1.5	0.2		0.2		
by propyl radical: $\text{CH}_3-\text{CH}_2-\text{H}_2\text{C}^\bullet + \text{R}'-\text{H} \leftrightarrow \text{R}'^\bullet + \text{CH}_3-\text{CH}_2-\text{CH}_3$													
23	C-C	2nd	14.9	6.1	13.5	14.9	-8.8	-1.4	0.0	12.3	0.0	12.3	<i>d</i>
24	C-C-C-C	2nd	4.8	-5.1	4.0	4.7	-9.9	-0.9	-0.1	12.2	-0.1	12.3	<i>d</i>
25	C-C-C-C	2nd	8.6	-0.8	7.7	8.7	-9.4	-1.0	0.0	10.9	0.0	10.9	<i>d, e</i>
26	C-C-C-C-C	2nd	2.9	-7.2	2.1	2.7	-10.1	-0.8	-0.2	10.2	-0.2	10.4	<i>d</i>
27	C=C-C	4th	37.3	32.3	35.9	37.5	-5.0	-1.4	0.2	9.9	0.2	9.8	<i>d</i>
28	C=C-C-C	4th	30.9	24.7	29.4	30.7	-6.2	-1.5	-0.2	8.0	-0.3	8.3	<i>d</i>
average absolute deviation							8.3	1.3	0.1		0.1		
by <i>i</i> -propyl radical: $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{H}_2\text{C}^\bullet + \text{R}'-\text{H} \leftrightarrow \text{R}'^\bullet + \text{CH}_3-\text{CH}_2-\text{CH}_3$													
29	C-C	2nd	13.6	4.9	12.5	13.8	-8.7	-1.1	0.2	13.2	0.2	13.0	<i>d, e</i>
30	C-C-C	2nd	8.6	-0.8	7.7	8.7	-9.4	-1.0	0.0	12.9	0.0	12.9	<i>d, e</i>
31	C=C-C	4th	35.2	29.8	33.8	35.2	-5.5	-1.4	0.0	9.7	0.0	9.7	<i>d</i>
average absolute deviation							7.9	1.2	0.1		0.1		
by benzyl radical: $\text{ph}-\text{H}_2\text{C}^\bullet + \text{R}'-\text{H} \leftrightarrow \text{R}'^\bullet + \text{ph}-\text{H}_3\text{C}$													
32	ph-C	5th	75.0	78.7	75.6	74.7	3.6	0.5	-0.3	15.5	-0.3	15.8	<i>c</i>
33	C=C-C	5th	67.5	70.5	68.6	67.8	3.0	1.1	0.3	15.8	0.3	15.5	<i>h</i>
34	ph-C-C	5th	68.7	71.5	69.4	68.6	2.8	0.7	-0.1	14.4	-0.1	14.5	<i>c</i>
35	tetralin	6th	66.4	65.5	64.3	66.4	-0.9	-2.1	0.0	13.2	0.0	13.2	<i>c</i>
36	ph-C-ph	5th	97.3	105.4	98.4	97.3	8.1	1.1	-0.1	12.7	-0.1	12.8	<i>c</i>
37	9,10-dihydrophenanthlene	6th	95.7	99.8	93.6	95.6	4.1	-2.1	-0.1	11.8	-0.1	11.9	<i>c</i>
38	(ph) ₃ -C	5th	123.2	136.1	124.7	123.2	12.9	1.5	0.0	11.0	0.0	11.0	<i>c</i>
39	fluorene	5th	102.8	112.1	104.2	102.9	9.3	1.3	0.1	10.7	0.1	10.6	<i>c</i>
40	9,10-dihydroanthracene	6th	95.0	99.3	93.2	95.2	4.3	-1.8	0.1	9.7	0.1	9.6	<i>c</i>
average absolute deviation							5.4	1.4	0.1		0.1		
for whole test set for 40 H abstraction reactions													
average absolute deviation							5.69	1.45	0.26		0.26		
expectation of deviation							-3.28	0.00	0.13		0.13		
standard deviation							5.70	1.64	0.50		0.50		
confidence interval (95%) of deviation							-14.5,	-3.2,	-0.9,		-0.9,		
							+7.9	+3.2	+1.1		+1.1		
for the test set, except methyl + <i>tert</i> -butane, ethyl + <i>tert</i> -butane, and methyl + methane													
average absolute deviation							5.82	1.36	0.14		0.14		
expectation of deviation							-3.11	-0.19	0.00		0.00		
standard deviation							5.93	1.50	0.18		0.18		
confidence interval (95%) of deviation							-14.7,	-3.1,	-0.35,		-0.35,		
							+8.5	+2.7	+0.35		+0.35		

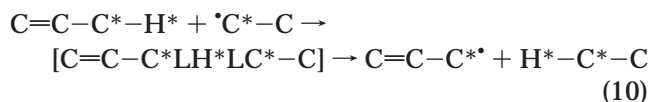
^a The carbon with underline is the carbon from which a hydrogen atom is abstracted. ^b Experimental E_a values from the references identified. When the values from different references are different, an arithmetic mean is used. ^c Reference 20. ^d Reference 46. ^e Reference 47. ^f Reference 45. ^g Reference 49. ^h Derived from the E_a value for the reverse reaction (ref 47). ⁱ Except methyl + *tert*-butane and methyl + methane. ^j Except ethyl + *tert*-butane.

paper.⁴¹ The experimental $\Delta H_f^\circ(\text{R}'-\text{H})$ values are from the literature.⁴⁸

Results and Discussion

1. Hydrogen Abstraction Reaction and Transition State Structure. A representative hydrogen abstraction reaction of ethyl radical and propene is as

follows:



where H* is the abstracting hydrogen atom. In this

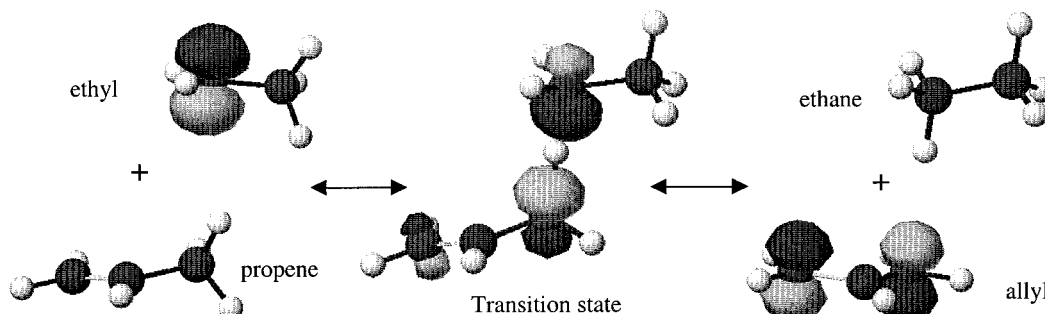


Figure 1. Conformation and SOMO of reactants, TS, and products for ethyl + propene reaction.

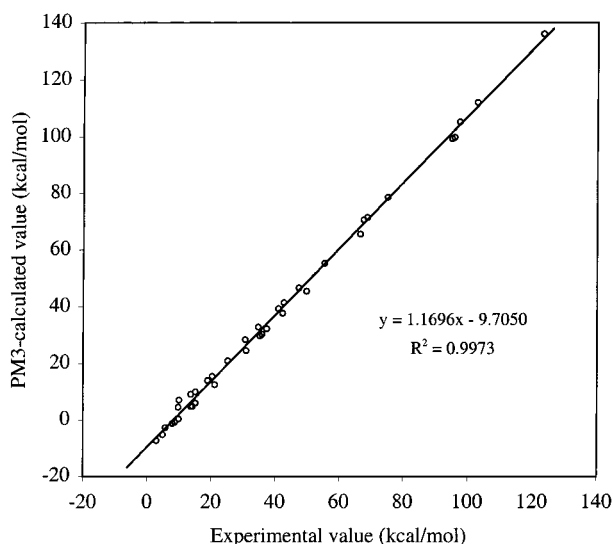


Figure 2. Comparison of PM3-calculated and experimental $\Delta H_f(TS)$ values for hydrogen abstraction reactions.

reaction, ethyl radical (hydrogen acceptor) abstracts the H^* from propene (hydrogen donor). The configurations and the singly occupied molecular orbitals (SOMO) corresponding to the reactants, transition state, and products are shown in Figure 1. The TS structure has linear, three-centered $C^*_{\text{propene}}-H^*-C^*_{\text{ethane}}$ bonds with pyramidal C atoms intermediate between sp^2 and sp^3 hybridization with bond lengths of 1.307 and 1.322 Å for $C^*_{\text{propene}}-H^*$ and $C^*_{\text{ethane}}-H^*$, respectively. This configuration indicates that the abstracting H^* takes a linear approach along the minimum energy path for the reaction. The SOMO presents the location of the unpaired electron. In the ethyl radical, the SOMO locates dominantly on the sp^2 C^* . In the TS structure, the SOMO is delocalized, distributing dominantly on the C^*_{propene} and C^*_{ethane} atoms. Interestingly, a small part of the SOMO locates on the end sp^2 C_{propene} atom, as shown in Figure 1. This indicates a π -conjugated TS structure, which reduces the total energy of the TS. For the allyl radical in the products, the SOMO distributes well on the two end C atoms, indicating a thoroughly π -conjugated radical structure.

2. Enthalpies of Transition States. The enthalpies of the transition states [$\Delta H_f(TS)$] for 40 hydrogen abstraction reactions were calculated by the PM3 method. The radicals involved in these reactions include the methyl, ethyl, propyl, *i*-propyl, and benzyl radicals. The H donors include alkyl-H, allylalkyl- H_α , and arylalkyl- H_α . The PM3-calculated results are listed in Table 1 in comparison with the experimental $\Delta H_f(TS)$ values. A considerable disagreement was found, as shown in Figure 2, with an average absolute deviation

of 5.69 kcal/mol for the test set, but the linear correlation between the PM3-calculated and experimental $\Delta H_f(TS)$ values is not bad, with an R^2 value of 0.9973. If one uses the regression equation, eq 11, obtained on the basis of the test set to scale the PM3-calculated $\Delta H_f(TS)$ values, as method proposed by Camaioni et al.,²⁰ the deviations of the estimated $\Delta H_f(TS)$ values from the experimental $\Delta H_f(TS)$ values decrease greatly (see Table 1). The average absolute deviation is 1.5 kcal/mol, with the maximum absolute deviation of 4.4 kcal/mol for the methyl + *tert*-butyl-H reaction.

$$\Delta H_{f,\text{calc}}(TS) = 1.1696\Delta H_{f,\text{exp}}(TS) - 9.7050 \quad (R^2 = 0.9973) \quad (11)$$

For convenience of discussion, we call this method the PM3-global-correlation (PM3-GC) method. Here, we should keep in mind that, for most of the hydrogen abstraction reactions involved in the test set, the activation energies change within a range of 7–16 kcal/mol and that the difference in E_a values between the H abstraction from an alkenyl- H_α and the H abstraction from an alkyl-H is only about 2 kcal/mol. Hence, the average absolute deviation of 1.5 kcal/mol for the E_a values from the PM3-GC method is still large and unsatisfactory for practical application in estimating the E_a values.

3. Family Correlation between the PM3-Calculated and Experimental $\Delta H_f(TS)$ Values. After carefully examining the TS structures and the correlation between the PM3-calculated and experimental $\Delta H_f(TS)$ values, we found that the 40 hydrogen abstraction reactions can be divided into six families according to the structural homology of the TSs and the correlations, as shown in Figures 3 and 4.

Methyl + Alkyl-H. The first family contains eight hydrogen abstraction reactions with methyl as a radical and alkyl-H species, including primary, secondary, and tertiary alkyl-H, as H donors. A very good linear correlation between the calculated and experimental $\Delta H_f(TS)$ values was found, as shown in Figure 3. The methyl + methyl-H and methyl + *tert*-butyl-H reactions show slightly higher positive deviations from the regression line, being 2.0 kcal/mol for both. The C atom in methane does not bond to any carbon atom, while *tert*-butyl-H is the only tertiary alkyl-H donor in the group. Such structural distinctions are probably the reason for the deviations from the regression line. The linear regression equation obtained by the least-squares fit for this family, excluding the methyl + methyl-H

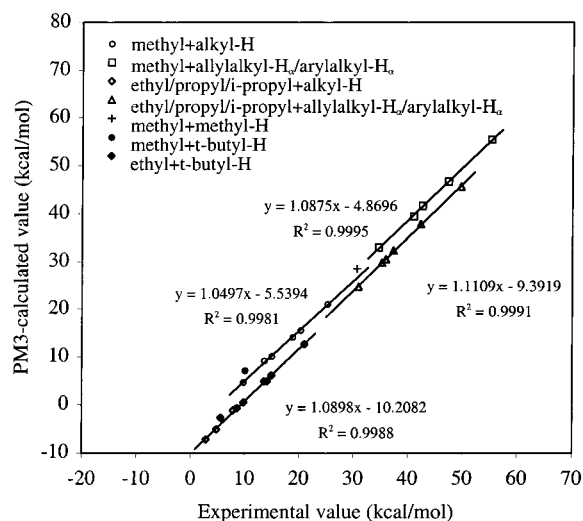


Figure 3. Family correlation between PM3-calculated and experimental $\Delta H_f(TS)$ values for alkyl + hydrocarbons reactions.

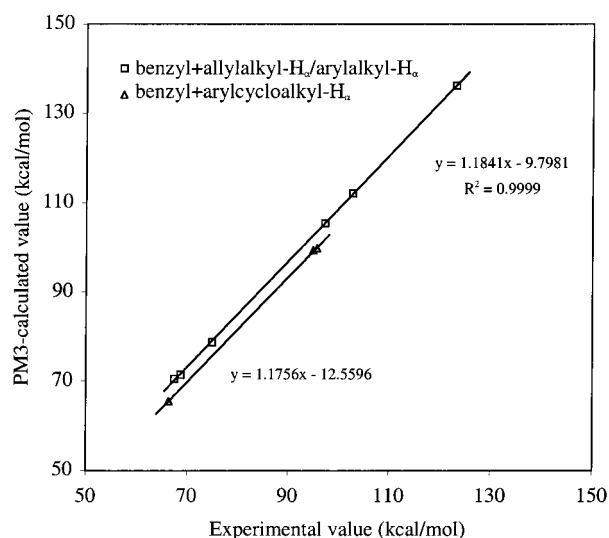


Figure 4. Family correlation between PM3-calculated and experimental $\Delta H_f(TS)$ values for benzyl + allylalkyl- H_α /arylalkyl- H_α and benzyl + arylcycloalkyl- H_α reactions.

and methyl + *tert*-butyl-H reactions, is

$$\Delta H_{f,calc}(TS) = 1.0497\Delta H_{f,exp}(TS) - 5.5394 \quad (R^2 = 0.9981) \quad (12)$$

Ethyl/Propyl/i-Propyl + Alkyl-H. The second family contains 12 hydrogen abstraction reactions with ethyl, propyl, or *i*-propyl as a radical and alkyl-H species as hydrogen donors. As shown in Figure 3, an excellent linear correlation between the PM3-calculated and experimental $\Delta H_f(TS)$ values was found for this group, with an R^2 value of 0.9988, except for the ethyl + *tert*-butyl-H reaction. The ethyl + *tert*-butyl-H reaction shows a slightly higher positive deviation (1.3 kcal/mol) from the regression line, similar to the methyl + *tert*-butyl-H reaction found in the first group. No significant effect of ethyl, propyl, and *i*-propyl radicals on the correlation is found, indicating that the effect of the primary and secondary radicals on the deviations is consistent or similar. The linear regression equation obtained by the least-squares fit for this family, excluding the ethyl + *tert*-butyl-H reaction, is given by eq 13.

$$\Delta H_{f,calc}(TS) = 1.0898\Delta H_{f,exp}(TS) - 10.2082 \quad (R^2 = 0.9988) \quad (13)$$

Methyl + Allylalkyl- H_α /Arylalkyl- H_α . The third family contains five hydrogen abstraction reactions with methyl as a radical. The H donors are allylalkyl- H_α or arylalkyl- H_α , in which the abstracting H bonds to the sp^3 C atom adjacent to a sp^2 C atom. Unlike the first family, the transition-state structures in this family have a common π -conjugation characteristic. An excellent linear correlation was found for this group, as shown in Figure 3. The linear regression equation obtained by the least-squares fit for this family is given by eq 14 with an R^2 value of 0.9995.

$$\Delta H_{f,calc}(TS) = 1.0875\Delta H_{f,exp}(TS) - 4.8696 \quad (R^2 = 0.9995) \quad (14)$$

Ethyl/Propyl/i-Propyl + Allylalkyl- H_α /Arylalkyl- H_α . The fourth family contains six hydrogen abstraction reactions with ethyl, propyl, or *i*-propyl as a radical. The H donors are allylalkyl- H_α or arylalkyl- H_α . All of the reactions in this family share the common characteristic that the H bonding to the sp^3 C atom adjacent to a sp^2 C atom is attacked by a primary or secondary alkyl radical, with a π -conjugated transition-state structure. Figure 3 shows an excellent linear correlation between the calculated and experimental $\Delta H_f(TS)$ values for this family. No significantly different effect from ethyl, propyl, and *i*-propyl radicals on the correlation is found, in agreement with the findings for the second family. The linear regression equation obtained by the least-squares fit for this family is given by eq 15 with an R^2 value of 0.9991.

$$\Delta H_{f,calc}(TS) = 1.1109\Delta H_{f,exp}(TS) - 9.3919 \quad (R^2 = 0.9991) \quad (15)$$

Benzyl + Allylalkyl- H_α /Arylalkyl- H_α . The fifth group contains six hydrogen abstraction reactions, in which benzyl is a π -conjugated radical and the hydrogen donors are allylalkyl- H_α or arylalkyl- H_α . A common characteristic of this family is that both the reactant radical and the product radical are the π -conjugated radicals. The benzyl radical has much lower activity than alkyl radicals because of the π -conjugation effect. As shown in Figure 4, the linear correlation between the PM3-calculated and experimental $\Delta H_f(TS)$ values is also excellent for this family. The regression equation obtained by the least-squares fit is given by eq 16 with an R^2 value of 0.9999.

$$\Delta H_{f,calc}(TS) = 1.1841\Delta H_{f,exp}(TS) - 9.7981 \quad (R^2 = 0.9999) \quad (16)$$

Benzyl + Arylcycloalkyl- H_α . The final family contains three hydrogen abstraction reactions with benzyl radical as a hydrogen acceptor. The H donors are partially hydrogenated polycyclic aromatics, including tetralin, dihydrophenanthrene, and dihydroanthracene, in which the abstracting H atom bonds to the sp^3 C atom in a hydrogenated ring and adjacent to one or more benzene-ring C atoms. The linear regression between the calculated and experimental $\Delta H_f(TS)$ values is excellent, as shown in Figure 4, although, of course, it must be noted that there are only three points. The obtained regression

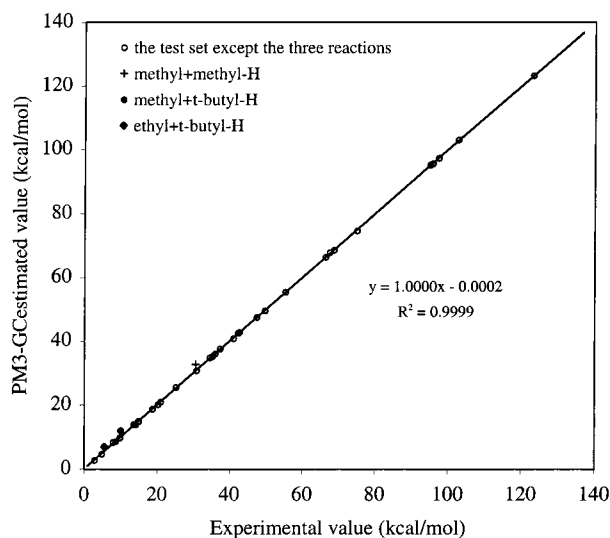


Figure 5. Comparison of PM3-FC-estimated and experimental $\Delta H_f^\circ(\text{TS})$ values for hydrogen abstraction reactions.

equation for this family is given by

$$\Delta H_{f,\text{calc}}^\circ(\text{TS}) = 1.1756\Delta H_{f,\text{exp}}^\circ(\text{TS}) - 12.5596 \quad (17)$$

The excellent family correlation observed above reflects clearly that the deviations between the PM3-calculated and the experimental values are systematic and dependent on the TS structures, resulting in the PM3 calculation giving similar estimation deviations for the structurally homologous TSs. Hence, the structurally homologous TSs show excellent linear correlations. The regression lines for the six families exhibit similar slopes, being 1.0497, 1.0898, 1.0875, 1.1109, 1.1841, and 1.1756. The intercepts of the lines are different from each other. The regression lines for the families with ethyl, propyl, or *i*-propyl radicals as hydrogen acceptors exhibit lower intercepts than those with methyl radicals as a hydrogen acceptor by about 5 kcal/mol, indicating that the families with ethyl, propyl, or *i*-propyl radicals have larger negative deviations from the experimental $\Delta H_f^\circ(\text{TS})$ values than the families with methyl radicals by this amount. These deviations are consistent with the deviation between the PM3-calculated and experimental enthalpies for the hydrocarbon radicals reported in previous studies,^{39,41} where the PM3-calculated enthalpy of the methyl radical shows a 5 kcal/mol negative deviation from the experimental value, while the PM3-calculated enthalpies of primary alkyl radicals show an ~ 11 kcal/mol negative deviation.

The family correlation found in this study allows one to improve the accuracy of the estimates by scaling the PM3-calculated $\Delta H^\circ(\text{TS})$ values. By using the regression parameters obtained from eqs 12–17 to scale the PM3-calculated $\Delta H_f^\circ(\text{TS})$ values, more accurate estimates are obtained, as shown in Table 1. We call this new method the PM3-family-correlation method (PM3-FC method). As shown in Figure 5, the PM3-FC-estimated $\Delta H_f^\circ(\text{TS})$ values are very well in agreement with the experimental values. The average absolute deviation and the standard deviation are 0.3 and 0.5 kcal/mol, respectively, for the entire test set.

4. Estimation of Activation Energies. On the basis of the transition state theory, the activation energies for the 40 hydrogen abstraction reactions were computed through eq 8 using the PM3-FC-estimated $\Delta H_f^\circ(\text{TS})$ values and the experimental $\Delta H_f^\circ(\text{R}^\bullet)$ and $\Delta H_f^\circ(\text{R}'-\text{H})$

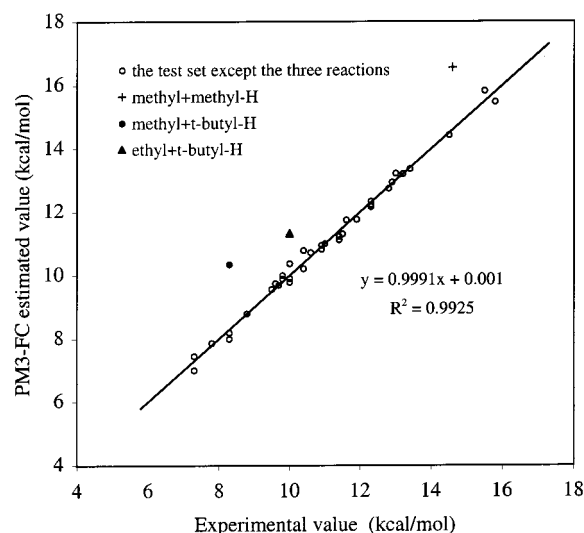


Figure 6. Comparison of PM3-FC-estimated and experimental activation energies for hydrogen abstraction reactions.

H) values. The results are given in Table 1. To compare the deviations of different methods, the deviations in the PM3 and PM3-GC methods were also calculated. In the PM3 method, the PM3-calculated $\Delta H_f^\circ(\text{TS})$, $\Delta H_f^\circ(\text{R}^\bullet)$, and $\Delta H_f^\circ(\text{R}'-\text{H})$ values were directly used for computing E_a by eq 8. In the PM3-GC method, the PM3-calculated $\Delta H_f^\circ(\text{TS})$ values were further scaled by using the regression equation (eq 11), and the experimental $\Delta H_f^\circ(\text{R}^\bullet)$ and $\Delta H_f^\circ(\text{R}'-\text{H})$ values were used. Statistical analysis of the deviation for each method was conducted. The results are listed in Table 1.

For estimation of E_a , the PM3 method has an average absolute deviation of 2.3 kcal/mol, with a standard deviation of 2.9 kcal/mol for the test set. The accuracy is better than that in the estimation of $\Delta H_f^\circ(\text{TS})$ by the PM3 method, because parts of the deviations in the PM3-calculated $\Delta H_f^\circ(\text{R}^\bullet)$, $\Delta H_f^\circ(\text{R}'-\text{H})$, and $\Delta H_f^\circ(\text{TS})$ values cancel each other in computing the E_a by eq 8. The PM3-GC method shows a lower average absolute deviation than the PM3 method, being 1.5 kcal/mol, with a standard deviation of 1.6 kcal/mol for the test set. Among the three methods, the PM3-FC method gives the least estimation deviation. Comparison of the PM3-FC-estimated and experimental E_a values is shown in Figure 6, with an average absolute deviation of 0.3 kcal/mol and a standard deviation of 0.5 kcal/mol for the test set. If the three special-case reactions, methyl + methyl-H, methyl + *tert*-butyl-H, and ethyl + *tert*-butyl-H, are excluded from the test set, the average absolute deviation and the standard deviation decrease to 0.1 and 0.2 kcal/mol, respectively. In other words, we can be 95% confident that the deviations between the PM3-FC-estimated and experimental values are in the interval of ± 0.4 kcal/mol for the test set, excluding the three special-case reactions. It is worth pointing out that the PM3-FC method not only has a higher accuracy than the semiempirical methods and the ab initio calculations currently reported for estimating the E_a , but also is a convenient and computationally cheap method because the semiempirical PM3 calculation is relatively simple and of low computational cost and can be used to calculate TS systems as large as those containing more than 100 C atoms.

It should be mentioned that the evaluation of the estimation methods in this study is based on the deviations of the estimated values from the experimen-

tal values recommended in the literature (see Table 1). The average absolute deviation of 0.3 kcal/mol for the whole test set indicates a derivation extent of the estimated values from the experimental values but does not indicate an average absolute error from the true values. Because in the PM3-FC method the PM3-calculated values were further corrected on the basis of the experimental values used in the regression analysis, the accuracy of the PM3-FC method is also dependent on the accuracy of the experimental values. The experimental values with higher accuracy will give more accurate regression parameters and then result in the estimated values with higher accuracy. The results from the deviation analysis imply that both the average absolute deviation and the standard deviation in the PM3-FC method are within the precision of most experiments for determining E_a .

Conclusions

The semiempirical PM3 calculations of transition state enthalpies for a test set of 40 hydrogen abstraction reactions involving hydrocarbons have been performed. The correlation of the PM3-calculated $\Delta H_f^\ddagger(\text{TS})$ values with the experimental values shows that the deviations are systematic for families of structurally related transition states. The TSs of the test hydrogen abstractions can be classified into six families according to their structural homology and the correlations between the PM3-calculated and experimental $\Delta H_f^\ddagger(\text{TS})$ values. Each family shows an excellent linear correlation. These findings allow one to calibrate the PM3-calculated $\Delta H_f^\ddagger(\text{TS})$ values by using the linear regression parameters, which leads to a very significant increase in estimation accuracy. The activation energies for the test set were estimated by using the calibrated $\Delta H_f^\ddagger(\text{TS})$ values on the basis of transition state theory. The average absolute deviation between the estimated and experimental activation energies is 0.3 kcal/mol, with a standard deviation of 0.5 kcal/mol. This study shows that the developed PM3-FC method has higher accuracy in estimating the activation energies of the hydrogen abstraction reactions involving hydrocarbons and is also a simple and computationally cheap method.

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