

ESTIMATING THE ACTIVATION ENERGY FOR HYDROGEN ABSTRACTION REACTIONS BY A SEMIEMPIRICAL CALCULATION

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INTRODUCTION

Free radical processes play very important roles in thermal chemistry in combustion, petroleum and coal coking, coal liquefaction and pyrolysis, oil shale retorting, thermal stability of fuels as well as free radical polymerization. One of the most important elementary reactions in free radical processes is hydrogen abstraction, which involves hydrogen transfer from a hydrogen donor to a hydrogen acceptor (a radical). In a companion paper [1], we have reported our approach to estimating the heats of formation of hydrocarbon radicals. In this paper, we will report our approach to the kinetics of free radical reactions. This work is focused on the estimation of activation energy (E_a) for hydrogen abstraction reactions. To obtain the activation energy of hydrogen abstraction reactions is very essential for the fundamental understanding of hydrogen transfer mechanism, and for the evaluation of hydrogen-donation abilities of hydrogen donors and hydrogen-acceptation ability of radicals. However, experimental methods to determine the activation energy are complicate and difficult, as the radicals are very unstable. Molecular simulation approaches to the hydrogen abstraction reactions have been reported [2-5]. By using the MNDO-PM3 method, Camaioni et al. calculated the heats of formation of the transition states ($\Delta H_f^\circ(\text{TS})$) for 22 hydrogen abstraction reactions [6]. From the correlation of experimental and calculated $\Delta H_f^\circ(\text{TS})$ values, they obtained a linear regression equation:

$$\Delta H_{f,\text{calcd}}^\circ(\text{TS}) = 1.143\Delta H_{f,\text{exptl}}^\circ(\text{TS}) - 8.256 \text{ kcal/mol} \quad (1)$$

In the present study, our objective was to develop a new method for estimating the activation energy (E_a) of the hydrogen abstraction reactions between hydrocarbon radicals and hydrocarbon compounds on the basis of the MNDO-PM3 calculation, experimental data from the literature, transition-state theory and statistical analysis.

COMPUTATIONAL METHODS

All quantum chemistry calculations in this study were performed by using a semiempirical method, MNDO-PM3 method [7,8], in CAChe MOPAC, Version 94. Geometry of the radicals was optimized by using EF method, and the corresponding heats of formation (ΔH_f°) of hydrocarbon free radicals were estimated by the method reported in the other our paper [1]. Geometry of the transition states was located by using the Saddle Calculation method followed by the Minimize Gradient method, and the corresponding $\Delta H_f^\circ(\text{TS})$ was calculated. Calculation of the activation energy is based on the transition-state theory:

$$E_a = \Delta H^\ddagger + (1-\Delta\nu^\ddagger) RT \quad (2)$$

The standard activation enthalpy (ΔH^\ddagger) was calculated by the equation (3):

$$\Delta H^\ddagger = \Delta H_f^\circ(\text{TS}) - \sum \Delta H_f^\circ \text{reactant} \quad (3)$$

For the bimolecular reaction, the $\Delta\nu^\ddagger$ value is -1.

SOURCES OF EXPERIMENTAL DATA

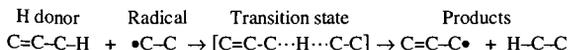
The experimental E_a values are from the available literature. As the data from different sources are somewhat inconsistent, we made the widest possible use of currently common and accepted experimental data. The main sources are from the reference 6 and 9. The experimental values of $\Delta H_f^\circ(\text{TS})$ were calculated by summing the activation enthalpy and ΔH_f° of the reactants:

$$\begin{aligned} \Delta H_{f,\text{exptl}}^\circ(\text{TS}) &= \Delta H^\ddagger + \sum \Delta H_f^\circ \text{reactant} \\ &= E_{a,\text{exptl}} - (1-\Delta\nu^\ddagger) RT + \sum \Delta H_f^\circ \text{reactant} \end{aligned} \quad (4)$$

RESULTS AND DISCUSSION

Hydrogen Abstraction Reaction

A representative hydrogen abstraction reaction of propene and ethyl radical is shown as follows:



In this reaction, ethyl radical (hydrogen acceptor) abstracts a hydrogen atom from propene (hydrogen donor). The corresponding configurations and spin densities for the reactants, transition state and products are shown in Figure 1. The TS structure has linear-centered C-H-C bonds with pyramidal C atoms intermediate between sp^2 and sp^3 with the bond length of 1.307 and 1.322 Å for $C_{\text{propene}}\text{-H}$ and $C_{\text{ethane}}\text{-H}$, respectively. The spin density indicates the location of the free radical (distribution of SOMO). In the TS structure, the radical is relocated on both C_{propene} and C_{ethane} atoms.

Heats of Formation of Transition States ($\Delta H^\ddagger(\text{TS})$)

The heats of formation of the transition states for 37 hydrogen abstraction reactions were calculated by the MNDO-PM3 method. The radicals involved in these reactions include alkyl, allyl and benzyl radicals.

As a whole, a considerable scatter exists, as shown in Figure 2 and 3, and the average error is ± 5.16 kcal/mol for the 37 transition states. However, we observed that the analogous reactions exhibit a very good linear correlation between experimental and calculated values. According to this observation, we can separate the 37 hydrogen abstraction reactions into 6 groups as follows:

Group	Radical	H donor
1	methyl	alkyl-H
2	methyl	alkenyl-H (or aryl-H)
3	ethyl (or propyl)	alkyl-H
4	ethyl (or propyl)	alkenyl-H (or aryl-H)
5	benzyl	alkyl-H or phenylalkyl-H
6	benzyl	partially hydrogenated polyaromatics

The least square fit was made for each group, with the R^2 values of 0.995, 0.999, 0.997, 0.995, 1.000 and 1.000, respectively. The group correlation reflects that the errors between PM3-calculated and experimental values are systematic and dependent on the reaction types. This finding allows one to be able to improve the accuracy of the estimates by scaling the $\Delta H^\ddagger(\text{TS})$ values calculated from MNDO-PM3 method. By using the regression parameters to scale the calculated $\Delta H^\ddagger(\text{TS})$, much accurate estimates are obtained with an average error of ± 0.33 kcal/mol for the 37 hydrogen abstraction reactions. We call this new method as PM3-systematical-correlation method (PM3-SC method).

Activation Energies for Hydrogen Abstraction Reactions

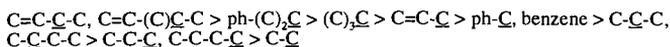
On the basis of the transition-state theory, the activation energies for the 37 hydrogen abstraction reactions have been estimated by the equation (2) using scaled $\Delta H^\ddagger(\text{TS})$ values. The estimated E_a in comparison with the experimental data from the literature are shown in Figure 4 for methyl, ethyl, propyl and benzyl as a hydrogen acceptor, respectively. In order to compare the errors from different estimation methods, the E_a values estimated by MNDO-PM3 method and Camaioni's method (using the linear regression (1) to scale the MNDO-PM3-calculated $\Delta H^\ddagger(\text{TS})$ values) are also shown in Figure 4. Statistical analysis of the errors for each method was conducted.

MNDO-PM3 method has an average error of ± 2.07 kcal/mol with the standard deviation of 2.71 kcal/mol. Camaioni's method shows lower average error than MNDO-PM3 method, being ± 1.69 kcal/mol with the standard deviation of 1.78 kcal/mol. In all three methods, our PM3-SC method gives the highest estimation accuracy with the average error of ± 0.24 kcal/mol and the standard deviation of 0.31 kcal/mol. In other words, with PM3-SC method, we can be 95 % confident that the difference between the estimated and experimental values is in the interval between -0.57 and $+0.63$ kcal/mol.

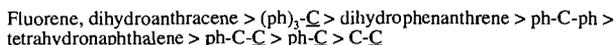
Evaluation of both Hydrogen-donation Ability of Hydrogen Donors and Hydrogen-acceptation Abilities of Radicals

The E_a value for hydrogen abstraction reactions is dependent on both the hydrogen-donation ability of hydrogen donors and the hydrogen-acceptation ability of the radicals. Using the same radical, the hydrogen-donation ability of the hydrogen donors is inversely proportional to the E_a ,

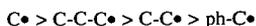
while using the same hydrogen donor, the hydrogen-accepting ability of the radical is inversely proportional to the E_a . Consequently, on the basis of analysis of the estimated E_a values for different hydrogen abstraction reactions, we can quantitatively evaluate both the hydrogen-donation ability of hydrogen donors and the hydrogen-accepting ability of radicals. By comparing the E_a values for hydrogen abstraction reactions with methyl radical as a hydrogen acceptor (the group 1 and 2), we can give the hydrogen-donation abilities of the hydrogen donors in the order as follows:



The underlined C atoms label the position of the donated hydrogen. By comparing the E_a values for hydrogen abstraction reactions with benzyl radical as a hydrogen acceptor (the group 5 and 6), we can give the hydrogen-donation abilities of other hydrogen donors in the order as follows:



On the other hand, by comparing the E_a values for hydrogen abstraction reactions using the same hydrogen donor (e.g. ethan) and different radicals, we can give the hydrogen-accepting abilities of the radicals in the order as follows:



Thus, we can use this method to expect quantitatively both the hydrogen-donation ability of other hydrogen donors and the hydrogen-accepting ability of other radicals.

CONCLUSIONS

After calculating $\Delta H^\ddagger(\text{TS})$ values for the 37 hydrogen abstraction reactions by MNDO-PM3 method and correlating them with the experimental data from the literature, it was found that the analogous reactions exhibit a very good linear correlation between experimental and calculated $\Delta H^\ddagger(\text{TS})$ values with the R^2 values higher than 0.994. On the basis of the MNDO-PM3 calculation, experimental data, transition state theory and statistical analysis, a new semiempirical method, PM3-SC method, has been developed to estimate the E_a for hydrogen abstraction reactions with an average error below ± 0.24 kcal/mol. The 95% confidence limits of the difference between the estimated and experimental E_a values is in the interval between -0.57 and +0.63 kcal/mol. The estimated E_a can be used to evaluate quantitatively the hydrogen-donation ability of hydrogen donors and the hydrogen-accepting ability of radicals.

ACKNOWLEDGMENTS

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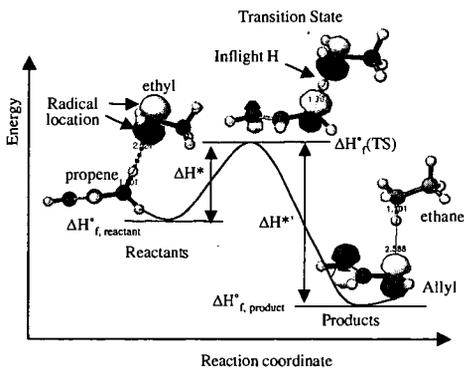


Figure 1 Configurations and spin densities for hydrogen abstraction reaction of propene and ethyl radical

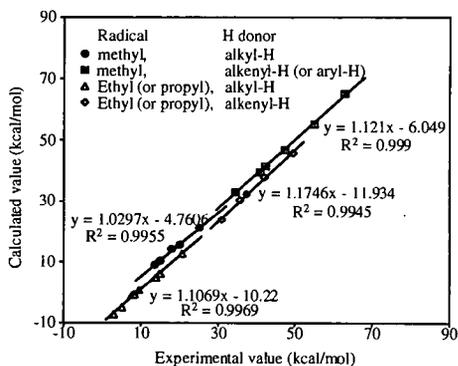


Figure 2 Systematic correlation of experimental and calculated $\Delta H^\circ_f(\text{TS})$ for H Abstraction with alkyl radicals as H acceptors

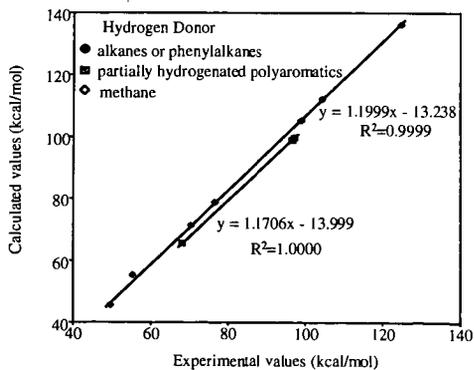


Figure 3 Systematic correlation of experimental and calculated $\Delta H^\circ_f(\text{TS})$ for H abstraction with phenyl radical as a H acceptor

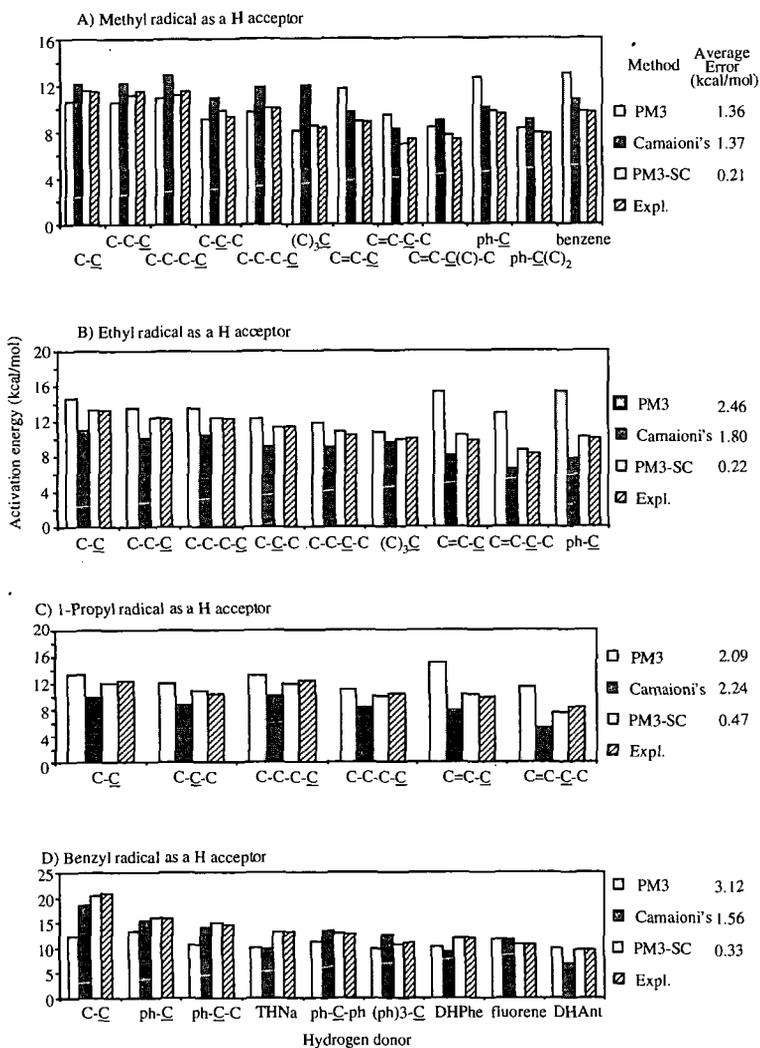


Figure 4 Experimental and estimated activation energies for H abstraction