

KINETICS OF 1, 3 HYDROGEN SHIFT OF ALKYL RADICAL REACTION CLASS: AN APPLICATION OF THE REACTION CLASS TRANSITION STATE THEORY

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TÓM TẮT

Bài báo này trình bày ứng dụng lý thuyết trạng thái chuyển tiếp của lớp phản ứng (RC-TST) để dự đoán hằng số tốc độ phản ứng chuyển vị hydro- 1,3 của một số hydrocarbon, đặc biệt là các gốc tự do. Dựa vào tính toán động học đơn giản chính xác, tất cả thông số tính toán theo phương pháp RC-TST kết hợp với phương pháp quan hệ năng lượng tuyến tính (Linear Energy Relationship (LER)) có thể tính toán được. Hằng số tốc độ phản ứng của bất kỳ phản ứng của loại này có thể được dự đoán từ năng lượng phản ứng tại mức BH&HLYP/cc-pVDZ. Các hằng số tốc độ phản ứng theo RC-TST/LER có thể so sánh với các giá trị tính toán trực tiếp sử dụng TST với phương pháp 1-dimension Eckart tunneling. Phương pháp RC-TST/LER là hữu hiệu để ước tính các hằng số tốc độ phản ứng cho phần lớn các phản ứng thuộc lớp phản ứng này.

ABSTRACT

This paper presents an application of the Reaction Class Transition State Theory (RC-TST) to predict rate constants for 1, 3-hydrogen shift reactions of some hydrocarbons, especially for alkyl radicals. Based on the accurate simple kinetic calculations, all parameters for the RC-TST method coupling with a Linear Energy Relationship (LER) can be derived. Thus, rate constants for any reaction in this class can be predicted from its reaction energy calculated at BH&HLYP/cc-pVDZ level. The RC-TST/LER rate constants are comparable to those calculated directly using the full TST with one dimension Eckart tunneling method. The RC-TST/LER method is efficient to estimate rate constants of a large number of reactions in this class.

1. INTRODUCTION

One of the goals of computational science is to predict observables where experiments have not yet been done or are difficult to carry out [1]. Besides, its result sometimes can suggest worthwhile future experiments. In the area of chemical kinetic theory, there has been much progress in developing direct ab-initio dynamics methods based on the transition state theory framework to calculate rate coefficients from first principles. These methods have achieved a rather excellent level of accuracy even for large biological systems. Among these methods, the simplest and most cost-effective one is the well-known Transition State Theory (TST), which requires only structural, energetic, and vibration frequency

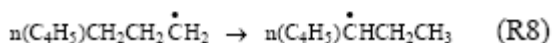
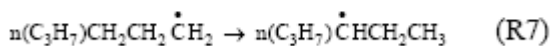
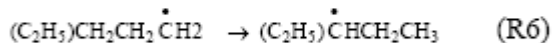
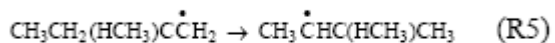
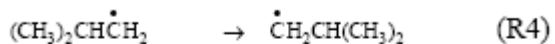
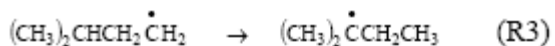
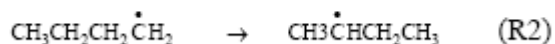
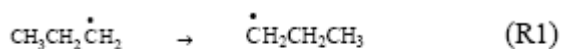
information at the reactant and transition state to calculate thermal rate constant.

For many combustion systems, detailed kinetic models [2] often consist of up to several thousands of elementary reactions whose kinetic parameters are mainly estimated from those available for similar reactions. It is impossible to obtain the kinetic data correctly for large number of reactions in such systems experimentally. It is still impractical to calculate thermal rate constants of every one of such reactions even with the simple TST method. The recently developed Reaction Class Transition State Theory (RC-TST) [2, 3], which is based on the transition state theory framework and properties of a reaction class in deriving the expression for relative rate constant, gives a cost-effective approach for

estimating the relative rate constants for a large number of reactions in a given class.

1, 3 Hydrogen shift reaction is a kind of radical isomerization reaction, one of the most important classes of reaction in combustion chemistry [4]. The principal (smallest) reaction in this class is $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{H}_2 \rightarrow \dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}_3$ and kinetic information for reactions involving larger hydrocarbons in this class is quite limited. However, such information is rather critical for modeling combustion of hydrocarbon fuels. In this study we have developed correlation expressions to estimate the rate coefficient of any reaction in this class relatively to the rate coefficient of principal reaction by using the RC-TST and Linear Energy Relationship (Evan-Polanyi linear relationship) [5, 6].

To estimate RC-TST/LER parameters for 1,3 hydrogen shift of alkyl radicals, some reactions are considered:



2. METHODOLOGY

2.1 Reaction Class Transition State Theory

Since reactions in the same class have the same reactive moiety, the difference between rate constants of any two reactions is mainly due to differences in the interactions between reactive moiety and their different substituents. In the RC-TST framework, rate constant of an arbitrary (denoted as R_a) is proportional to rate constant of principal reaction (the smallest reaction in the class denoted as R_p) of the same class by a temperature dependent function $f(T)$:

$$k_a(T) = f(T)k_p(T) \quad (1)$$

$$\text{With } f(T) = f_\sigma f_K f_Q f_V \quad (2)$$

Where f_σ , f_K , f_Q , f_V are symmetry number, tunneling, partition function and potential energy factors, respectively. These factors are simply the ratios of corresponding components in the TST expression for the two reactions:

$$f_\sigma = \frac{\sigma_a}{\sigma_p} \quad (3)$$

$$f_K(T) = \frac{k_a(T)}{k_p(T)} \quad (4)$$

$$f_Q(T) = \frac{\left(\frac{Q_a^\ddagger(T)}{\Phi_a^\ddagger(T)} \right)}{\left(\frac{Q_p^\ddagger(T)}{\Phi_p^\ddagger(T)} \right)} = \frac{\left(\frac{Q_a^\ddagger(T)}{Q_p^\ddagger(T)} \right)}{\left(\frac{\Phi_a^\ddagger(T)}{\Phi_p^\ddagger(T)} \right)} \quad (5)$$

$$f_V(T) = \exp \left[-\frac{(\Delta V_a^\ddagger - \Delta V_p^\ddagger)}{k_B T} \right] = \exp \left[-\frac{\Delta \Delta V^\ddagger}{k_B T} \right] \quad (6)$$

Where $K(T)$ is transmission coefficient accounting for quantum mechanical tunneling effects; σ is reaction symmetry number; Q and Φ are total partition functions (per unit volume) of the transition state and reactants, respectively; ΔV^\ddagger is classical reaction barrier height; T is temperature in Kelvin; k_B and h are Boltzmann and Planck constants, respectively. The potential energy factor can be calculated by using reaction barrier heights of arbitrary reaction and principal reaction. The classical reaction barrier heights ΔV^\ddagger for arbitrary reaction can be obtained using the Linear Energy Relationship (LER), between classical barrier heights and reaction energies of reactions in a given reaction class without having to calculate it explicitly.

The principle task of this paper is to determine the explicit expressions for these factors linking the rate constants of R_p and those of R_a in the same class.

2.2 Computational methods

All of the electronic structure calculations were carried out using the program package GAUSSIAN 98. Geometries and frequencies of reactants, transition states, and products were optimized at the BH&HLYP level of

theory with the cc-pVDZ basis set because BH&HLYP has been found previously to be sufficiently accurate for predicting transition state properties for hydrogen abstraction or shift reactions by a radical [7,8]. This information was used to derive the RC-TST factors. Besides, BH&HLYP/cc-pVDZ reaction energies were then used to derive the LER's between barrier height and reaction energy.

The TST rate constants, tunneling factors, and partition function factors were calculated employing kinetic module of the web-based CSEO program [9].

3. RESULTS AND DISCUSSION

In this part, we first describe how RC-TST factors and the LER's were derived. Subsequently, several error analyses were performed in order to provide some estimates on the uncertainty of the RC-TST/LER method. This is done by comparisons between rate constants of the considered reactions predicted from the RC-TST/LER method and those from full TST calculations.

3.1 Calculation of symmetry number factor

Since the reaction symmetry numbers for reactions R_a and R_p are known, this factor is determined exactly [10].

3.2 Calculation of tunneling ratio factor

The tunneling factor $K(T)$ is the ratio of tunneling coefficients of the target and principal reactions. It can be accurately calculated using the one dimension Eckart tunneling method, which only needs the imaginary frequencies, and the forward and reverse barrier heights of both reactions. It is observed in this study that tunneling factors for 1, 3 hydrogen shift are rather similar (see Fig. 1.) and thus can be assumed to be the same. We choose a factor to represent for all values in this class. In particular, when $T \geq 500K$, $K(T)$ is chosen by 1 and when $T \leq 500K$, tunneling factors of $R5/R1$ ($fK5$) is used to represent those in this class by fitting it with calculated values:

$$f_k(T) = 7,2350118 \cdot 10^{-5} + 0,10429124T - 6,5542563 \cdot 10^{-4}T^2 + 1,4196136 \cdot 10^{-6}T^3 - 1,0355073 \cdot 10^{-9}T^4 \quad (7)$$

The standard deviation coefficients for these fits are larger than 0.998. Moreover, it can be seen that the ratio f_k is comparable to those with the direct Eckart calculation using reaction information from BH&HLYP/cc-pVDZ. The higher the temperature, the smaller the absolute error.

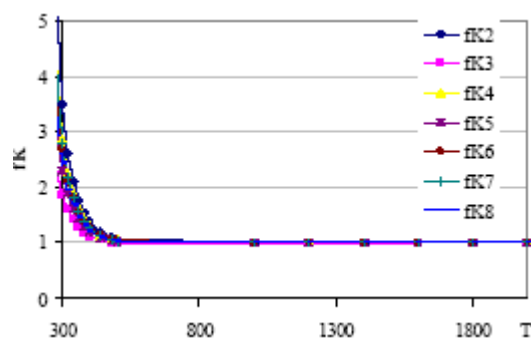


Fig.1 Plot of the tunneling factor f_k as functions of temperature for 1, 3 shift of hydrogen

3.3 Calculation of partition function factor

Partition function factors for 8 reactions in the class calculated in the temperature range 300-2000K and all ratios are given in Fig 2. Similar to tunneling factor, the partition function factor for this class can be approximated by the ratio of $R7$ and $R1$ with the following function:

$$f_Q = 0,023470026 - 0,0001062115 \cdot 7T - 4,7052393 \cdot 10^{-9}T^2 + 3,9183397 \cdot 10^{-10}T^3 \quad (8)$$

which gives the maximum error of about 70% and the mean absolute error less than 35% for all reactions from 300K to 2000K.

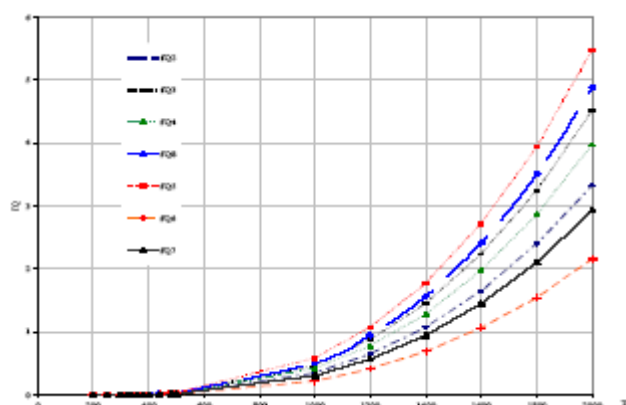


Fig.2 Plot of partition function factor f_Q as function of temperature for all 8 reactions considered.

3.4 Calculation of potential energy factor

The potential energy factor f_V can be easily calculated using eq. (6) where ΔV_a^\ddagger and ΔV_b^\ddagger are the barrier heights of the arbitrary and the principal reactions, respectively. The reaction barrier heights of any reaction in this class can be obtained by utilizing the LER between the reaction energy and the reaction barrier height. The reaction barrier heights are plotted against reaction energies, both of which were calculated at the BH&HLYP/cc-pVDZ. The linear relationship was plotted in Fig. 3 and the fitted expressions were also obtained using the least squared method given below:

$$\Delta V^\ddagger = 45.706439 + 0.65713508 E \quad (\text{kcal/mol}) \quad (9)$$

The absolute deviations of reaction barrier heights between the LER and full quantum calculations are smaller than 3kJ/mol. The mean absolute deviation of reaction barrier heights predicted from BH&HLYP reaction energies is 1.45kJ/mol. These deviations are in fact smaller than the systematic errors of the computed reaction barriers from full electronic structure calculations.

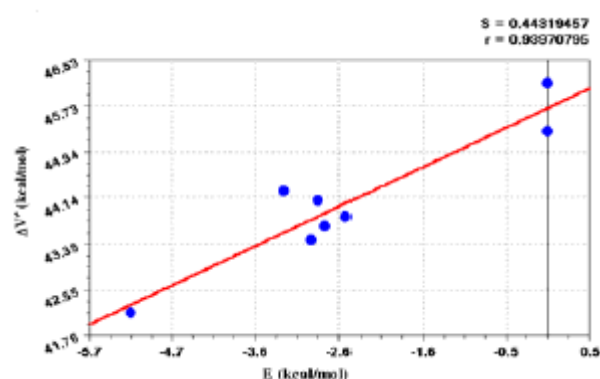


Fig.3 Linear energy relationship plots of barriers heights ΔV^\ddagger versus reaction energies E

3.5 Rate constants of the Principal reaction

Rate constants of the principal reaction had been previously calculated by TST with Eckart tunnel. The thermal rate constants (s^{-1}) are given by:

$$k_p = 3407.10^{-55} T^{19.20978} \cdot \exp(-1799.43/T) \quad (10)$$

This expression is used for the considered reaction class.

3.6 Predictions of rate constants

All necessary parameters have been estimated - namely symmetry number factor, tunneling factor, partition function factor and potential energy factor - to apply the RC-TST theory to predict rate constants for any reaction in 1, 3 hydrogen shift class. By combining with the linear relationship between the reaction energy and the reaction barrier height, only the reaction energy is needed and it can be obtained at the BH&HLYP/cc-pVDZ. The procedure to calculate rate constants of an arbitrary reaction in this class is: 1) calculate the symmetry number factor from eq. (3); 2) approximate tunneling ratio factor and partition function factor using eq. (7), (8), respectively; 4) calculate the potential energy factor using eq. (6). The reaction barrier height can be obtained using eq. (9) for reaction energies, 5) rate constant of the arbitrary reaction can be calculated by taking the product of the principal reaction rate constant given by eq. (10) with the four factors above.

To determine the overall efficiency of the RC-TST method, we performed two analyses.

One is to compare the calculated rate constants of the reactions with those from direct measurements or derived from other experimental data and theoretical simulations. Since there has been no experimental data for any reaction of this class up to now, alternatively, we compared the calculated rate constants for a small number of reactions using both RC-TST/LER and full TST/Eckart methods in the first analysis and the result is presented in Fig.4. Here we plotted the relative deviation defined by $(|k_{\text{TST/Eckart}} - k_{\text{RC-TST/LER}}|/k_{\text{RC-TST/LER}})$ percent versus temperature for several selected reactions. The relative errors are less than 100% for all test cases. This is certainly an acceptable level of accuracy for reaction engineering purposes.

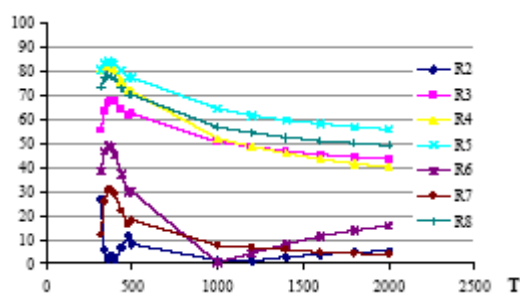


Fig.4 Relative deviations as functions of temperature between rate constants calculated from the RC-TST/LER and full TST/Eckart methods.

The other is to examine the internal errors in different factors in the RC-TST/LER methods in the second analysis. The total internal error is affected by the errors in the approximation of tunneling factor, partition function factor and potential energy factor used in the method. The results of the error analysis from these different relative rate factors are shown in Fig. 5.

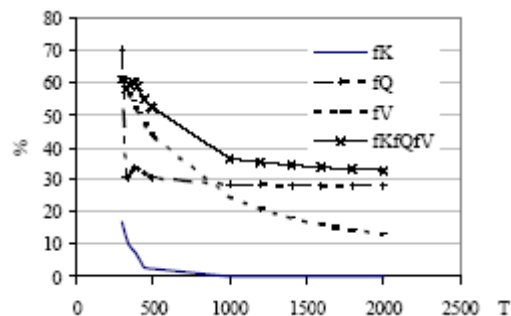


Fig.5 Average absolute errors of the total relative rate factors $f(T)$ (eq. 2) and its components, namely the tunneling (f_K), partition function (f_Q) and potential energy (f_V) factors as functions of temperature.

In this figure, we plotted the absolute errors averaged over all 8 reactions as functions of temperature. Errors from all components are less than 72% for the temperature range from 300 to 1000K. The errors tend to decrease when temperature increases. The fact that total internal errors occurring in the relative rate factor is less than 75% shows that RC-TST/LER is an excellent extrapolation method for estimating rate constants of any reactions in this class from that of the principal reaction.

4. CONCLUSION

We have presented an application of the reaction class transition state theory in conjunction with the linear energy relationship (RC-TST/LER) to predict thermal rate constants of the reaction class 1, 3 hydrogen shifts of alkyl radicals. The RC-TST/LER method is shown to be both simple and effective for rate constant prediction of any reaction in a given class from only the reaction energy that can be calculated at BH&HLYP. Detailed analysis shows that the systematic errors in the calculated rate constants arising from approximations used in the RC-TST/LER method are less than 80%.

Table 1. Calculated symmetry number factors

Reaction	Symmetry number factor
R1	1
R2	1
R3	1
R4	1
R5	1
R6	1
R7	1
R8	1

Table 2. Ab initio derived parameters and formulations of the RC-TST/LER method for 1, 3 hydrogen shift alkyl radical reaction class

	$k(T) = f_{\sigma} f_K(T) f_Q(T) f_V(T) k_p(T)$ $f_V(T) = \exp\left\{-\frac{(\Delta V^{\ddagger} - \Delta V_p^{\ddagger})}{k_B T}\right\}$
f_{σ}	(See Table 1 for example)
$f_K(T)$	$f_K(T) = 1$ when $T \geq 500K$ $f_K(T) = 7,2350118 \cdot 10^{-5} + 0,10429124 T - 6,5542563 \cdot 10^{-4} T^2 + 1,4196136 \cdot 10^{-6} T^3 - 1,0355073 \cdot 10^{-9} T^4$ when $T < 500K$
$f_Q(T)$	$f_Q = 0,023470026 - 0,0001062115 T - 4,7052393 \cdot 10^{-9} T^2 + 3,9183397 \cdot 10^{-10} T^3$
$\Delta V_{\ddagger}^{\ddagger}$ (kcal/mol)	$\Delta V^{\ddagger} = 45,706439 + 0,65713508 E$
ΔV_p^{\ddagger} (kcal/mol)	45,706439
$k_p(T), s^{-1}$	$k_p = 3407 \cdot 10^{-55} \cdot T^{19,20978} \cdot \exp(-1799,43/T)$

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