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Kinetics of the Hydrogen Abstraction OH + Alkane → H_2O + Alkyl Reaction Class: An Application of the Reaction Class Transition State Theory[†]

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This paper presents an application of the reaction class transition state theory (RC-TST) to predict thermal rate constants for hydrogen abstraction reactions of the type OH + alkane → HOH + alkyl. We have derived all parameters for the RC-TST method for this reaction class from rate constants of 19 representative reactions, coupling with linear energy relationships (LERs), so that rate constants for any reaction in this class can be predicted from its reaction energy calculated at either the AM1 semiempirical or BH&HLYP/cc-pVDZ level of theory. The RC-TST/LER thermal rate constants for selected reactions are in good agreement with those available in the literature. Detailed analyses of the results show that the RC-TST/LER method is an efficient method for accurately estimating rate constants for a large number of reactions in this class. Analysis of the LERs leads to the discovery of the β-carbon radical stabilization effect that stabilizes the transition state of any reaction in this class that yields products having one or more β-carbons, and thus leads to the lower barrier for such a reaction.

1. Introduction

Recent advances in computational science and computer technology have made great impacts on science. Their main goal is to predict observables where experiments have not been done or are difficult to carry out. These results sometimes can suggest worthwhile future experiments. In the area of chemical kinetics, one of the simplest and most cost-effective methods for calculating rate constants is the well-known transition state theory (TST),[1,2] which requires only structural, energetic, and vibrational frequency information for reactants and the transition states to calculate thermal rate constants. On the basis of this TST framework, much progress has been made in developing direct ab initio dynamics methods for calculating rate constants from first principles.[3−9]

For many combustion systems, detailed kinetic models[10−14] often consist of up to several thousands of elementary reactions whose kinetic parameters are mainly estimated from those available for similar reactions. To correctly model the physical behaviors of such systems, it is critical to have accurate kinetic parameters. However, it is impossible to obtain the kinetic data correctly for the large number of reactions in such systems experimentally. It is still impractical to calculate thermal rate constants for every such reaction even with the simple TST method. The recently developed reaction class transition state theory (RC-TST),[9,15,16] which is based on the transition state theory framework and the properties of a reaction class in deriving the expression for relative rate constants, gives a cost-effective approach for estimating the relative rate constants for a large number of reactions in a given class. The RC-TST method is based on the concept that reactions in a given class, having the same reactive moiety, have similar potential energy surfaces along the reaction coordinate and thus such information can be extrapolated from one to the others. Furthermore, within a given reaction class, it is usually observed that there is a linear energy relationship (LER) between barrier heights and reaction energies. Combining both facts, the RC-TST/LER theory provides a rigorous methodology for estimating thermal rate constants of any reaction only from its reaction energy, which can be calculated from a relatively low level of theory such as a semiempirical molecular orbital method. This is in the spirit of the thermochemical kinetics formulation of the conventional transition state theory (TST) proposed earlier by Cohen[17] to analyze available experimental rate constants and to propose an approximate scheme for extrapolating thermal rate constants to a wider temperature range for a small number of reactions in the H + RH reaction class.

The reaction class concept was also employed by Green and co-workers[18,19] for developing group additivity (GA) contributions of transition states in estimating the thermal rate constants of reactions in a given class. Although both the RC-TST/LER method and the group additivity (GA) method are based on the TST framework and utilize the same reaction class concept, there are inherent differences in the two methodologies for obtaining thermal rate constants. The RC-TST/LER method takes advantage of the similarities in the potential surfaces of reactions in the same class to achieve cancellations in obtaining the *relative* rate constants. The thermal rate constant of any reaction in the class can be calculated from its reaction energy and the rate constants of the reference reaction. Thus, one can think of the RC-TST/LER method as a procedure for extrapolating rate constants of the reference reaction to rate constants of any reaction in the class. The GA method, on the other hand, takes advantage of the similarity in the reactive moiety of reactions in the same class to define a "supergroup" for the transition states. The GA method can calculate *absolute* thermal rate

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constants without requiring any further information. In other words, the GA method is a parametrization procedure for a specific reaction class.

Hydrogen abstraction of saturated hydrocarbons by the hydroxyl radical is one of the most important classes of reactions in combustion chemistry. This can be indicated by the more than 70 experiments and theoretical studies in the literature for the smallest reaction in this class, namely, the $OH + CH_4 \rightarrow HOH + CH_3$ reaction. However, kinetic information for reactions involving larger hydrocarbons, for example, larger than C_5, in the OH + alkane → HOH + alkyl class is limited. For example, for the hydrogen abstraction at normal hexane, there are five direct experimental studies, four of which are in the range 298−390 K and only one at 962 K, and only three theoretical studies for the temperature range 298−500 K.[20] For modeling the combustion of hydrocarbon fuels, especially for large hydrocarbons in commercial fuels such as kerosene and gasoline, kinetic information for the temperature range from 300 to 2000 K is needed. In this study, we applied the RC-TST/LER method to derive all parameters for estimating the rate constants of any reaction belonging to this class. To do so, our main task is to find the analytical correlation expressions for rate constants between reactions in a small representative set of the class and the reference one. Within the RC-TST/LER methodology, these correlation expressions are applicable to all reactions in the class, and thus, the relative rate constants of any reaction in the class can be estimated relative to the rate coefficient of the reference reaction.

To develop RC-TST/LER parameters for the HO + alkane class, 19 reactions including the principal reaction are considered as a representative set. These reactions are given below.

$$OH + CH_4 \rightarrow H_2O + \mathbf{C}H_3 \qquad (R_1)$$

$$OH + CH_3CH_3 \rightarrow H_2O + \mathbf{C}H_2CH_3 \qquad (R_2)$$

$$OH + CH_3CH_2CH_3 \rightarrow H_2O + \mathbf{C}H_2CH_2CH_3 \qquad (R_3)$$

$$\rightarrow H_2O + CH_3\mathbf{C}HCH_3 \qquad (R_4)$$

$$OH + CH_3CH_2CH_2CH_3 \rightarrow H_2O + \mathbf{C}H_2CH_2CH_2CH_3 \qquad (R_5)$$

$$\rightarrow H_2O + CH_3\mathbf{C}HCH_2CH_3 \qquad (R_6)$$

$$OH + (CH_3)_2CHCH_3 \rightarrow H_2O + (CH_3)_2CH\mathbf{C}H_2 \qquad (R_7)$$

$$\rightarrow H_2O + (CH_3)_3\mathbf{C} \qquad (R_8)$$

$$OH + CH_3CH_2CH_2CH_2CH_3 \rightarrow H_2O + \mathbf{C}H_2CH_2CH_2CH_2CH_3 \qquad (R_9)$$

$$\rightarrow H_2O + CH_3\mathbf{C}HCH_2CH_2CH_3 \qquad (R_{10})$$

$$\rightarrow H_2O + CH_3CH_2\mathbf{C}HCH_2CH_3 \qquad (R_{11})$$

$$OH + (CH_3)_2CHCH_2CH_3 \rightarrow H_2O + \mathbf{C}H_2(CH_3)CHCH_2CH_3 \qquad (R_{12})$$

$$\rightarrow H_2O + (CH_3)_2\mathbf{C}CH_2CH_3 \qquad (R_{13})$$

$$\rightarrow H_2O + (CH_3)_2CH\mathbf{C}HCH_3 \qquad (R_{14})$$

$$\rightarrow H_2O + (CH_3)_2CHCH_2\mathbf{C}H_2 \qquad (R_{15})$$

$$OH + (CH_3)_2CHCH_2CH_2CH_3 \rightarrow H_2O + (CH_3)_2CH\mathbf{C}HCH_2CH_3 \qquad (R_{16})$$

$$OH + (CH_3)_2CHCH_2CH(CH_3)_2 \rightarrow H_2O + (CH_3)_2CH\mathbf{C}HCH(CH_3)_2 \qquad (R_{17})$$

$$OH + (C_2H_5)_2CHCH_3 \rightarrow H_2O + (C_2H_5)_2\mathbf{C}CH_3 \qquad (R_{18})$$

$$OH + (C_2H_5)_3CH \rightarrow H_2O + (C_2H_5)_3\mathbf{C} \qquad (R_{19})$$

where reactions R_1, R_2, R_3, R_5, R_7, R_9, R_{12}, and R_{15} are hydrogen abstraction reactions at primary carbons; R_4, R_6, R_{10}, R_{11}, R_{14}, R_{16}, and R_{17} are at secondary carbons; and R_8, R_{13}, R_{18}, and R_{19} are at tertiary carbons; here, bold C letters represent radical sites as in the products of hydrogen abstraction reactions.

2. Methodology

Reaction Class Transition State Theory. Since the details of the RC-TST/LER method have been presented elsewhere,[9,15,16] we discuss only its main features here. It is based on the realization that reactions in the same class have the same reactive moiety; thus, the difference between the rate constants of any two reactions is mainly due to differences in the interactions between the reactive moiety and their different substituents. Within the RC-TST framework, the rate constant of an arbitrary reaction (denoted as k_a) is proportional to the rate constant of a reference reaction (k_r) (note that one often would choose the reference reaction to be the smallest reaction in the class, which is referred to as the principal reaction) in the same class by a temperature dependent function, $f(T)$:

$$k_a(T) = f(T) \times k_r(T) \qquad (1)$$

The rate constants for the reference reaction are often known experimentally or can be calculated accurately from first principles. The key idea of the RC-TST method is to factor $f(T)$ into different components under the TST framework:

$$f(T) = f_\sigma \times f_\kappa \times f_Q \times f_V \qquad (2)$$

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

$$f_\sigma = \frac{\sigma_a}{\sigma_r} \qquad (3)$$

$$f_\kappa(T) = \frac{\kappa_a(T)}{\kappa_r(T)} \qquad (4)$$

$$f_Q(T) = \frac{\left(\dfrac{Q_a^\ddagger(T)}{\Phi_a^R(T)}\right)}{\left(\dfrac{Q_r^\ddagger(T)}{\Phi_r^R(T)}\right)} = \frac{\left(\dfrac{Q_a^\ddagger(T)}{Q_r^\ddagger(T)}\right)}{\left(\dfrac{\Phi_a^R(T)}{\Phi_r^R(T)}\right)} \qquad (5)$$

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

where $\kappa(T)$ is the transmission coefficient accounting for the quantum mechanical tunneling effects; σ is the reaction symmetry number; $Q^{\ddagger}$ and Φ^{R} are the total partition functions (per unit volume) of the transition state and reactants, respectively; $\Delta V^{\ddagger}$ is the classical reaction barrier height; T is the temperature in Kelvins; and k_B and h are the Boltzmann and Planck constants, respectively. The potential energy factor can be calculated using the reaction barrier heights of the arbitrary reaction and the reference reaction. The classical reaction barrier heights ($\Delta V^{\ddagger}$) for the 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 them explicitly. It is worth mentioning that, within the RC-TST framework, the variational effects to account for recrossing are only implicitly included in the rate constants of the reference reaction and are not explicitly included in the calculations of the reaction class factors.

The main tasks of this paper are the following: (1) to determine the explicit expressions for these factors linking the rate constants of R_r and those of R_a in the same class using a small representative set of reactions in the class as mentioned earlier and (2) to provide error analyses of the results. Once these expressions are determined, thermal rate constants of any reaction in this class can be predicted from only its reaction energy needed for the LER expression.

Computational Details. All of the electronic structure calculations were carried out using the Gaussian 98 program.[21] A hybrid nonlocal density functional theory (DFT), particularly Becke's half-and-half[22] (BH&H) nonlocal exchange and Lee−Yang−Parr[23] (LYP) nonlocal correlation functionals, has been found previously to be sufficiently accurate for predicting the transition state properties for hydrogen abstraction reactions by a radical.[7,8,24,25] Note that, within the RC-TST framework, as discussed above, only the relative barrier heights are needed. Our previous studies have shown that the relative barrier heights can be accurately predicted by the BH&HLYP method.[15,26] The geometries of reactants, transition states, and products were optimized at the BH&HLYP level of theory with Dunning's correlation-consistent polarized valence double-ζ basis set [3s2p1d/2s1p] denoted as cc-pVDZ,[27] which is sufficient to capture the physical change along the reaction coordinate for this type of reaction. Frequencies of the stationary points were also calculated at the same level of theory. This information was used to derive the RC-TST factors. The AM1 semiempirical method was also employed to calculate the reaction energies of those reactions considered here. AM1 and BH&HLYP/cc-pVDZ reaction energies were then used to derive the LERs between the barrier heights and reaction energies. Note that the AM1 reaction energy is only used to extract an accurate barrier height from the LERs; it is not directly involved in any rate calculations.

TST/Eckart rate constants for all reactions in the above representative reaction set were calculated employing the kinetic module of the web-based Computational Science and Engineering Online (CSE-Online) environment.[28] In these calculations, overall rotations were treated classically and vibrations were treated quantum mechanically within the harmonic approximation except for the modes corresponding to the internal rotations of the CH_3 and OH groups, which were treated as the hindered rotations using the method suggested by Ayala et al.[29] Thermal rate constants were calculated for the temperature range 300−3000 K, which is sufficient for many combustion applications such as premixed flame and shock-tube simulations. RC-TST parameters are derived from these rate constant calculations.

3. Results and Discussion

In the discussion below, we first describe how the LERs and the RC-TST factors were derived using the above training reaction set. Subsequently, several error analyses were performed in order to provide some estimates on the accuracy of the RC-TST/LER method applied to this reaction class. The first error analysis is the direct comparison between the calculated rate constants with those available in the literature for the R_3−R_8 reactions. The second error analysis is the comparisons between rate constants calculated by the RC-TST/LER method and those from explicit full TST/Eckart calculations for the whole training set. The final analysis is on the systematic errors caused by introducing approximations in the RC-TST/LER method.

The first task for applying the RC-TST/LER method to any reaction class is to select the reference reaction. In our previous studies,[15,16] we suggested the use of the smallest reaction, that is, the principal reaction of the class to be the reference reaction, since its rate constants can be calculated accurately from first principles or are often known experimentally. However, in this study, we found that the principal reaction is not always the best reference reaction. In fact, for this reaction class, we found that the hydrogen abstraction OH + C_2H_6 reaction is a better reference reaction than the principal OH + CH_4 reaction for the following reasons. CH_4 is known to have strange behaviors compared to other saturated hydrocarbons due to its lack of a C−C bond, which exists in larger hydrocarbons. For example, the reaction barrier of reaction R_1 is appreciably larger by at least 3 kcal/mol than those of other reactions in the class as discussed later. In addition, on the basis of our analyses of both reactions of OH with methane and ethane, it is shown that the OH + C_2H_6 reaction gives a better correlation than the OH + CH_4 reaction, especially for the partition function factors. For these reasons, the reaction between hydroxyl and ethane (R_2) is selected as the reference reaction for the OH + alkane reaction class in this study.

Rate Constants of the Reference OH + C_2H_6 → HOH +C_2H_5 Reaction. In our previous study,[16] we pointed out that the rate constants for the reference reaction do not have to be calculated from first principles but could be taken from experimental data. For the OH + C_2H_6 reaction, rate constants suggested from a review study by Baulch et al.[30] are close to the most recent experimental data by Krasnoperov and Michael[31] (the maximum deviation is 15% at 2000 K). These suggested rate constants are valid over a wide range of temperatures from 250 to 2000 K and thus are selected for the application of the RC-TST/LER method here. These rate constants can be expressed as

$$k_r = 1.06 \times 10^{-12} \times \left(\frac{T}{298K}\right)^{2.00} \times \exp\left(-\frac{860(\text{cal/mol})}{RT}\right), \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \quad (7)$$

Potential Energy Factor. The potential energy factor can be calculated using eq 6, where $\Delta V_a^{\ddagger}$ and $\Delta V_r^{\ddagger}$ are the barrier heights of the arbitrary and reference reactions, respectively. It is known that in order to achieve an accuracy on the order of 1 kcal/mol in the classical barrier height for radical reactions such as those in the reaction class considered here, a rather high level of electronic structure theory such as CCSD(T) or better and with a sufficiently large basis set is required. However, we have shown that the differences in the barrier heights for reactions in a given class can be accurately calculated at a lower

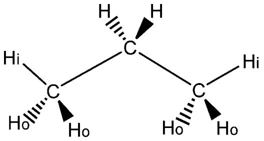

Figure 1. Two types of hydrogen atoms, namely, the in-plane (H_i) and out-of-plane (H_o), of the primary carbon of propane.

level of theory such as DFT methods, particularly the BH&HLYP level for this study.[32] In fact, we also have shown that within a given class there is a linear energy relationship (LER) between the barrier height and the reaction energy, similar to the well-known Evans−Polanyi linear free energy relationship.[33−35] Thus, with such a LER, accurate barrier heights can be predicted from only the reaction energies. In this study, the LER is determined where the reaction energy can be calculated by either the AM1 or BH&HLYP level of theory.

Before discussing the determination of LERs for this reaction class, it is important to point out a minor complication discovered by Hu et al.[36] that for alkanes larger than ethane, such as propane (C_3H_8, see Figure 1), the three hydrogen atoms of the primary carbon are not equivalent for abstraction by an OH radical and thus the barrier heights of reactions at non-equivalent hydrogen atoms are different. In fact, there are two types of hydrogen atoms in this case; specifically, one is the hydrogen atom in the same plane of the carbon chain denoted as H_i in Figure 1 and the other is the two hydrogen atoms out of this plane denoted as H_o. The difference in the barrier heights of the two types of hydrogen is found to be about 1.0 kcal/mol at the BH&HLYP/cc-pVDZ level of theory. It is noted that the partition functions at the transition state for each hydrogen type are also different. For simplicity within the RC-TST/LER methodology, we assume that abstractions of hydrogen atoms at the primary carbon have the same rate with the barrier height taken to be the average value of those at the three hydrogen positions. For the more complicated cases such as for reaction R_{12} where there are six different positions of hydrogen, the representative barrier height is also assumed to be the average value. Similar approximations are used for calculating other reaction class factors in this case. The errors from such approximations are parts of the systematic errors of the RC-TST/LER method that will be discussed later. It is worth mentioning that reaction energies corresponding to the abstraction at different hydrogen atoms at the primary carbon site of propane are different by, at most, about 0.4 kcal/mol and the average value was used in the determination of parameters of the RC-TST/LER method.

TABLE 1: Reaction Energies, Barrier Heights, and Absolute Deviations between Calculated Barrier Heights from DFT and Semiempirical Calculations and Those from LER Expressions (Energies Are in kcal/mol)

	ΔE		$\Delta V^\ddagger$			$\lvert\Delta V^\ddagger - \Delta V^\ddagger_{\mathrm{LER}}\rvert$[e]	
reaction	DFT[a]	AM1[b]	DFT[a]	DFT[c]	AM1[d]	DFT[c]	AM1[d]
R_1	−4.26	−21.15	9.65	9.54	9.30	0.11	0.36
R_2	−8.21	−26.98	6.84	7.00	7.01	0.16	0.16
R_3	−7.59	−26.84	6.26	6.25	5.91	0.01	0.35
R_4	−11.48	−32.25	4.82	4.89	4.94	0.07	0.12
R_5	−7.68	−26.86	6.21	6.19	5.90	0.02	0.31
R_6	−11.27	−32.01	3.89	3.89	3.88	0.01	0.01
R_7	−7.68	−26.29	5.89	6.20	6.12	0.31	0.23
R_8	−14.17	−36.65	3.28	3.16	3.21	0.12	0.07
R_9	−7.68	−26.86	6.15	6.19	5.90	0.04	0.25
R_{10}	−11.32	−32.04	3.83	3.85	3.87	0.03	0.04
R_{11}	−11.07	−31.65	3.20	3.02	2.85	0.18	0.35
R_{12}	−7.77	−26.27	5.81	6.13	6.13	***0.33***	0.33
R_{13}	−13.79	−36.44	2.29	2.26	2.14	0.03	0.15
R_{14}	−11.46	−31.61	3.69	3.76	4.04	0.07	0.34
R_{15}	−8.61	−27.06	5.68	5.60	5.82	0.08	0.14
R_{16}	−11.29	−31.39	2.96	2.88	2.95	0.09	0.01
R_{17}	−10.94	−30.76	2.87	3.11	3.20	0.24	0.34
R_{18}	−13.55	−35.45	1.71	1.43	1.36	0.28	0.35
R_{19}	−12.90	−35.22	1.72	1.84	1.45	0.12	0.27
MAD[f]						**0.12**	**0.22**

[a] Calculated at the BH&HLYP/cc-pVDZ level of theory. [b] Calculated at the AM1 level of theory. [c] Calculated from the LER using reaction energies calculated at the BH&HLYP/cc-pVDZ level of theory (eq 8). [d] Calculated from the LER using reaction energies calculated at the AM1 level of theory (eq 9). [e] $\Delta V^\ddagger$ from BH&HLYP/cc-pVDZ calculations; $\Delta V^\ddagger_{\mathrm{LER}}$ from the linear energy relationship using BH&HLYP/cc-pVDZ and AM1 reaction energies. [f] Mean absolute deviations (MADs) for all reactions R_1−R_{19}.

The reaction energies and barrier heights for all representative reactions using different methods are given in Table 1. It is noted that, since barrier heights for the 19 reactions in the training set are given explicitly in Table 1, other relationships using different levels of theory for calculating the reaction energy can also be derived. The reaction barrier heights calculated at the BH&HLYP/cc-pVDZ level and the observed linear energy relationships plotted against the reaction energies calculated at the BH&HLYP/cc-pVDZ and AM1 levels are shown in parts a and b of Figure 2, respectively. From the observed LERs, we discovered an electronic effect referred to as β-radical stabilization; that is, the existence of alkyl groups at the β-positions from the radical position of the product alkyl would noticeably stabilize the transition state and thus lower the barrier for hydrogen abstraction. The degree of stabilization does not depend on the size of the alkyl group nor the number of alkyl substitutions at a given β-carbon position but rather depends on the number of β-carbon positions. This can be illustrated by three parallel lines in both parts of Figure 2, where the top line is for production of alkyls having no β-carbon, the middle line is for those having one β-carbon position, and the bottom line is for those having at least two β-carbon positions. It is observed that the effect of the number of β-carbon positions on the barrier heights is different. The first two β-carbon positions have a noticeable effect by lowering the barrier by about 1 kcal/mol, while the third β-carbon has a negligible contribution. This can be seen by the decreasing differences in the three lines for product having no β-carbon positions to those having at least two β-carbon positions. These lines were obtained using the least-squares fitting method for the three cases above using the barrier heights and reaction energies calculated at the BH&HLYP/cc-pVDZ level of theory, and they have the following expressions in the energy units of kilocalories per mole:

$$\Delta V^\ddagger_{\mathrm{a}} = 0.644 \times \Delta E_{\mathrm{a}} + 12.284 \text{ for products having no } \beta\text{-carbon} \quad (8a)$$

$$\Delta V^\ddagger_{\mathrm{a}} = 0.644 \times \Delta E_{\mathrm{a}} + 11.140 \text{ for products having } \textit{one } \beta\text{-carbon position} \quad (8b)$$

$$\Delta V^\ddagger_{\mathrm{a}} = 0.644 \times \Delta E_{\mathrm{a}} + 10.150 \text{ for products having at least } \textit{two } \beta\text{-carbon positions} \quad (8c)$$

The fitting expressions using barrier heights at the BH&HLYP/

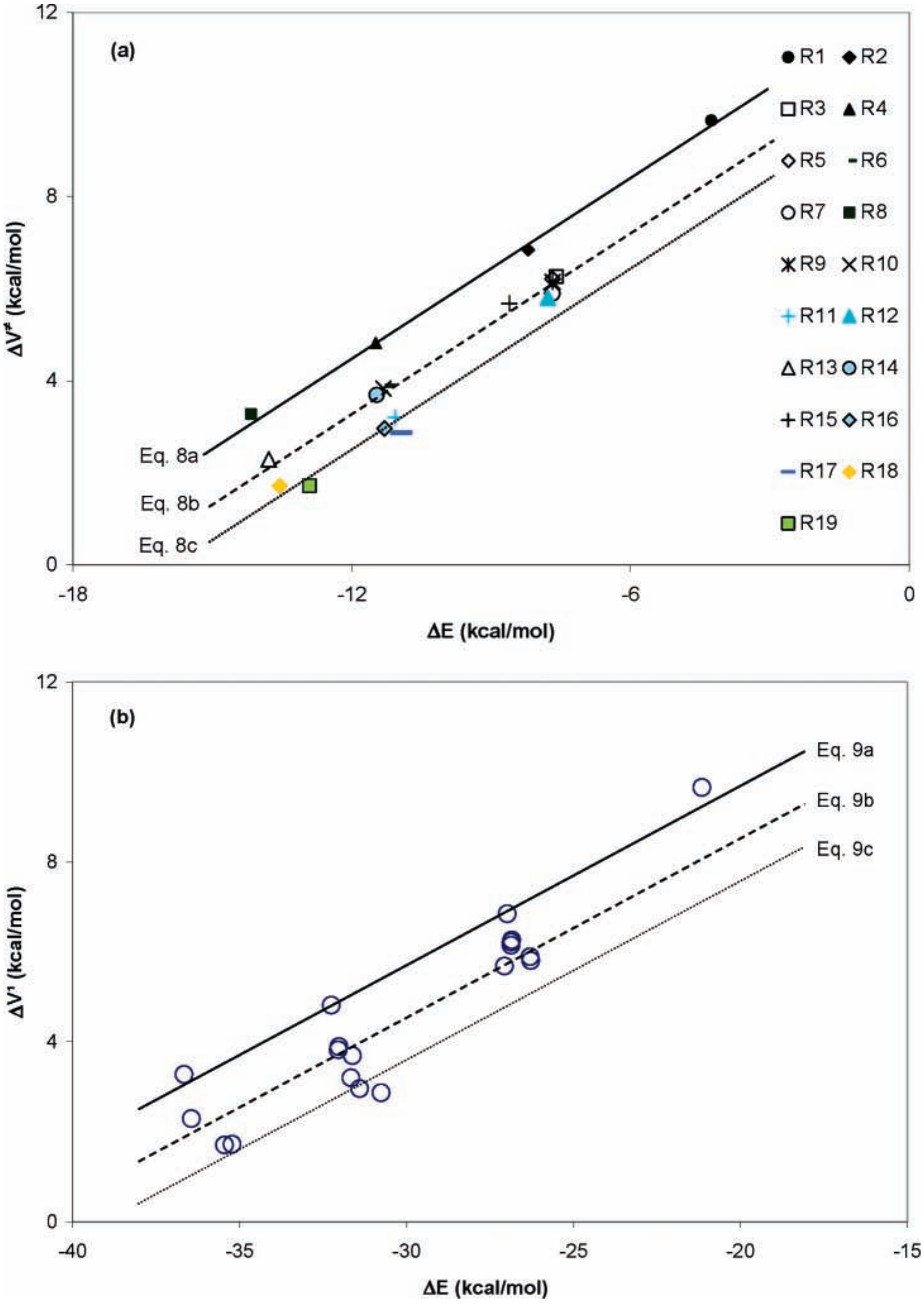

Figure 2. Linear energy relationship plots of the barrier heights ($\Delta V^{\ddagger}$) versus the reaction energies (ΔE). Barrier heights were calculated at the BH&HLYP/cc-pVDZ level of theory. ΔE's were calculated at the (a) BH&HLYP/cc-pVDZ and (b) AM1 levels of theory.

cc-pVDZ level and reaction energies at the AM1 level of theory are also given as

$$\Delta V_a^{\ddagger} = 0.393 \times \Delta E_a + 17.600 \text{ for products having no } \beta\text{-carbon} \quad (9a)$$

$$\Delta V_a^{\ddagger} = 0.393 \times \Delta E_a + 16.447 \text{ for products having } \textit{one } \beta\text{-carbon position} \quad (9b)$$

$$\Delta V_a^{\ddagger} = 0.393 \times \Delta E_a + 15.280 \text{ for products having at least } \textit{two } \beta\text{-carbon positions} \quad (9c)$$

The absolute deviations of reaction barrier heights between the LERs and the direct DFT BH&HLYP/cc-pVDZ calculations are smaller than 0.33 kcal/mol (see Table 1). The mean absolute deviation of reaction barrier heights predicted from BH&HLYP and AM1 reaction energies are 0.11 and 0.22 kcal/mol, respectively. These deviations are in fact smaller than the systematic errors of the computed reaction barriers from full electronic structure calculations. Note that in the RC-TST/LER methodology only the relative barrier height is needed. To compute these relative values, the barrier height of the reference reaction R_2 calculated at the same level of theory, that is, BH&HLYP/cc-pVDZ, is needed and has a value of 6.84 kcal/mol (see Table 1).

Symmetry Number Factor. The symmetry number factors (f_{σ}) were calculated simply from the ratio of reaction symmetry numbers of the arbitrary and reference reactions using eq 3 and are listed in Table 1. The reaction symmetry number of a reaction is known as the statistical number counting the number of symmetry equivalent reaction paths. It can be easily calculated from the rotational symmetry numbers of the reactant and the

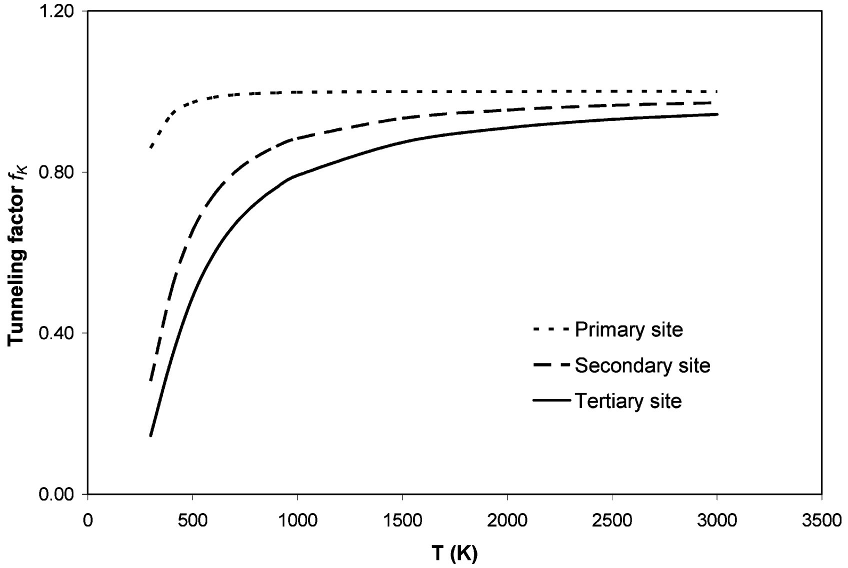

Figure 3. Plot of the tunneling factors (f_κ) as a function of temperature for abstractions of hydrogen from primary (dotted line), secondary (dashed line), and tertiary (solid line) carbon sites.

transition state;[37] thus, this factor is calculated exactly. It is worth noting that the scaling from rate constants at an individual hydrogen of a particular carbon site to the total rate constants by the reaction symmetry number would be exact if rate constants at different hydrogen positions were the same. As mentioned above, these hydrogen positions are not equivalent in some cases. However, since we introduced an "averaged" approach as discussed in the potential factor above, these hydrogen positions are equivalent in the calculation of the symmetry factor.

Tunneling Factor. The tunneling factor (f_κ) is the ratio of the transmission coefficient of reaction R_a to that of reaction R_r. Although absolute transmission coefficients for hydrogen abstraction reactions having the H−L−H (heavy−light−heavy) reaction type often require multidimensional tunneling methods to account for the large corner-cutting effects often observed for these types of reactions, such effects are not very large due to the relatively low barrier heights for reactions in this class. Furthermore, due to cancellation of errors in calculations of the tunneling factors, we have shown that such a factor, f_κ, can be reasonably estimated using the one-dimensional Eckart method.[38] The tunneling calculations are based on the average barrier heights and reaction energies as discussed in the previous part. Calculated results for the representative set of reactions can then be fitted to an analytical expression. It was observed in this study as well as in our previous work[16] that tunneling factors for hydrogen abstraction reactions at the same sites—primary, secondary, or tertiary carbon sites—are rather similar and thus can be assumed to be the same for each carbon site. Simple expressions for the three tunneling factors for abstraction at the primary, secondary, and tertiary carbon sites, respectively, are obtained by fitting to the calculated values and are given below:

$$f_\kappa = 1.0011 \times [1 - \exp(-0.0068 \times T)] \quad \text{for primary carbon sites} \quad (10a)$$

$$f_\kappa = 1.9807 \times [0.4811 - \exp(-0.0037 \times T)] \quad \text{for secondary carbon sites} \quad (10b)$$

$$f_\kappa = 1.7143 \times [0.5373 - \exp(-0.0027 \times T)] \quad \text{for tertiary carbon sites} \quad (10c)$$

TABLE 2: Calculated Symmetry Number Factors and Tunneling Factors at 300 K

reaction	symmetry no. factor	tunneling ratio factor (f_κ) Eckart[a]	fitting[b]	deviation[c]	% deviation[d]
R_2	1.000	(12.95)[f]			
R_3	1.000	0.88	0.86	0.02	2.6
R_4	0.333	0.35	0.28	0.07	20.4
R_5	1.000	0.86	0.86	0.00	0.2
R_6	0.667	0.29	0.28	0.01	4.2
R_7	1.500	0.85	0.86	0.01	1.4
R_8	0.167	0.17	0.15	0.02	12.2
R_9	1.000	1.00	0.86	***0.14***	14.4
R_{10}	0.667	0.27	0.28	0.01	5.4
R_{11}	0.333	0.22	0.28	0.06	***27.1***
R_{12}	1.000	0.84	0.86	0.02	1.8
R_{13}	0.167	0.12	0.15	0.02	16.2
R_{14}	0.333	0.27	0.28	0.01	3.7
R_{15}	0.500	0.72	0.86	0.14	19.2
R_{16}	0.333	0.26	0.28	0.02	8.0
R_{17}	0.333	0.25	0.28	0.03	12.4
R_{18}	0.167	0.13	0.15	0.02	11.7
R_{19}	0.167	0.14	0.15	0.01	3.7
MAD[e]				**0.04**	**9.7**

[a] Calculated directly using the Eckart method with BH&HLYP/cc-pVDZ reaction barrier heights and energies. [b] Calculated by using a fitting expression (see eq 10). [c] Absolute deviation between the fitting and directly calculated values. [d] Percentage deviation (%). [e] Mean absolute deviations (MADs) and deviation percentage between the fitting and directly calculated values. [f] Tunneling coefficient calculated for reaction R_2 using the Eckart method with the energetic and frequency information at BH&HLYP/cc-pVDZ.

The correlation coefficients for these fits are larger than 0.999. The three equations are plotted in Figure 3. It is noticed that, although the transmission coefficient for a reaction decreases as the temperature increases, the tunneling factor, a relative factor, increases when the temperature is raised. Moreover, for any given temperature, the tunneling factors increase when changing from a tertiary site to secondary and primary sites. This can be explained by the differences in reaction barrier heights and the imaginary frequencies of these reactions. Table 2 also lists the error analysis of tunneling factors at 300 K. It can be seen that the same tunneling factor expression can be reasonably assigned to those reactions at the same site with the largest absolute deviation of 0.14 for R_9 and R_{15}, the largest percentage deviation of 27.1% for R_{11}, and the mean absolute

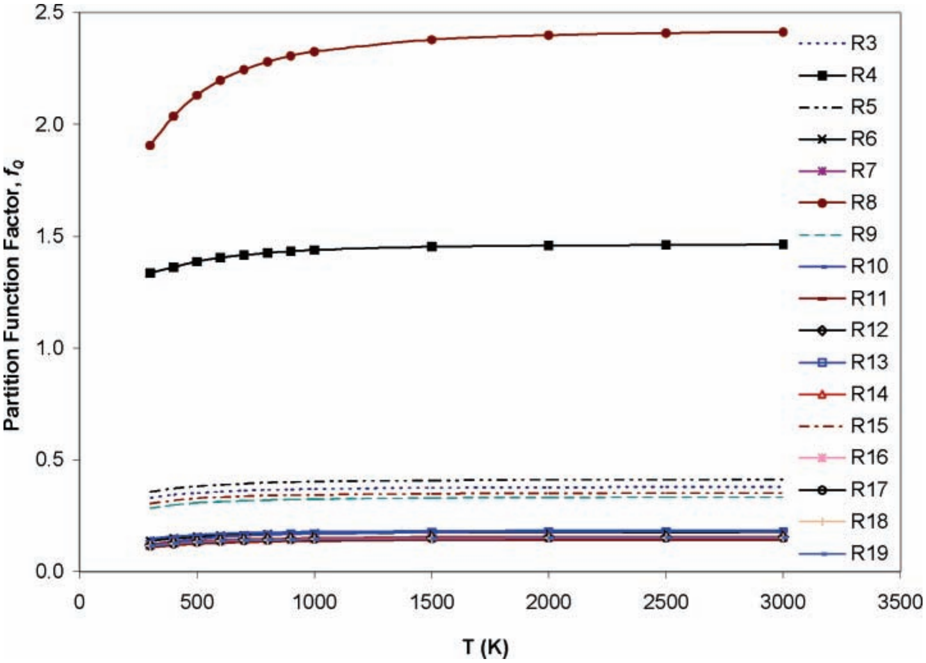

Figure 4. Plot of the partition function factor (f_Q) as a function of temperature for all 17 considered reactions (R_3−R_{19}).

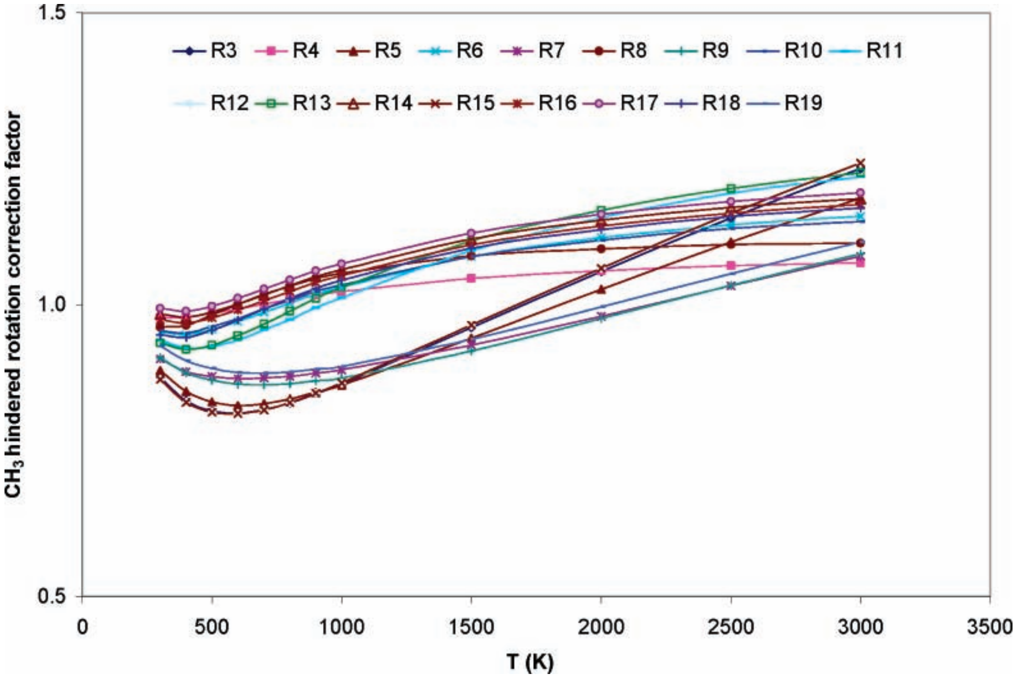

Figure 5. Hindered rotation correction factors for rotation of CH_3 groups as a function of temperature for selected reactions.

deviation of 9.7%, compared to the direct Eckart calculation using reaction information from the BH&HLYP/cc-pVDZ level of theory. At higher temperatures, tunneling contributions to the rate constants decrease and thus, as expected, the differences between the approximated values and the explicitly calculated ones also decrease; for example, the maximum error for all reactions is less than 10% at 500 K. Since the absolute tunneling coefficients of the three cases approach unity at different rates as the temperature increases, the relative tunneling factors also approach unity at different rates, as shown in Figure 3.

Partition Function Factor. As pointed out in our previous study,[16] the partition function factor (f_Q) mainly originates from the differences in the coupling between the substituents with the reactive moiety and its temperature dependence arises from the vibrational component only. Partition function factors based on the harmonic approximation for 17 reactions (for reactions R_3−R_{19}) in the class in the temperature range 300−3000 K are given in Figure 4. It can be seen that these partition function factors gather into two main groups. Group I consists of all reactions that yield products having no β-carbon or those occurring at a primary carbon site and its corresponding product having only one β-carbon position. Group II consists of the remaining cases. The partition function factors for reactions belonging to group I can be approximated by an average value

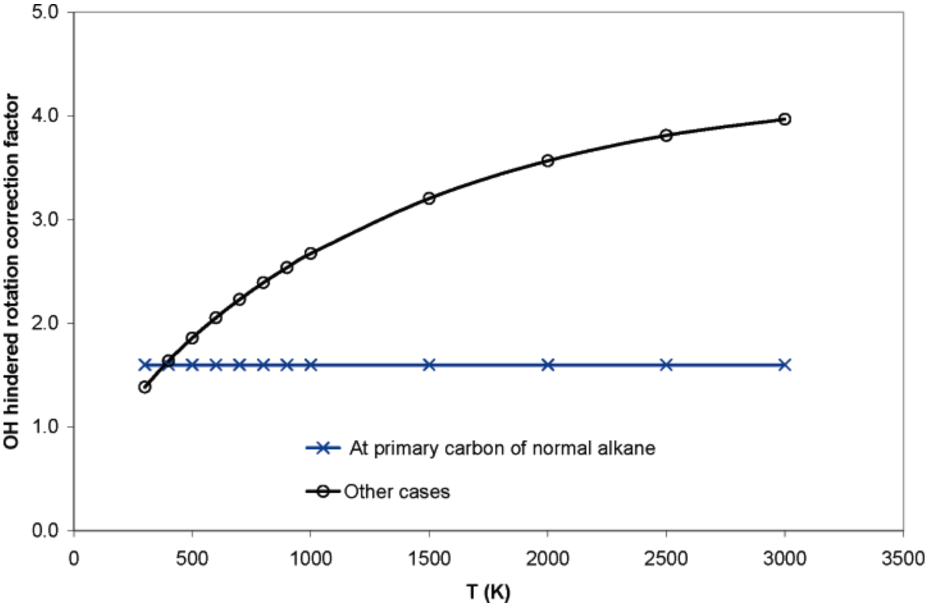

Figure 6. Approximate hindered rotation correction factors for rotation of the OH group as a function of temperature (see eqs 12a and 12b).

TABLE 3: Parameters and Formulations of the RC-TST/LER Method for the OH + Alkane → H_2O + Alkyl Reaction Class

	$k(T) = f_\sigma \times f_\kappa(T) \times f_Q(T) \times f^{\mathrm{HR}}(T) \times f_\nu(T) \times k_r(T)$; $f_\nu(T) = \exp[-(\Delta V^\ddagger - \Delta V_r^\ddagger)/k_B T]$	
	T is in Kelvins; $\Delta V^\ddagger$ and ΔE are in kilocalories per mole	
f_σ	calculated explicitly from the symmetry of reactions (see Table 1)	
$f_\kappa(T)$	$1.0011 \times [1 - \exp(-0.0068 \times T)]$ for primary carbon $1.9807 \times [0.4811 - \exp(-0.0037 \times T)]$ for secondary carbon $1.7143 \times [0.5373 - \exp(-0.0027 \times T)]$ for tertiary carbon	
$f_Q(T)$	0.35 for reactions that yield products having no β-carbon OR reactions at a primary carbon site with products having one β-carbon 0.15 for other cases	
$f^{\mathrm{HR}}(T)$	1.60 for reactions at primary site of normal alkane $0.0390 \times 0.9998^T \times T^{0.6338}$ for other cases	
$\Delta V^\ddagger$	ΔE at BH&HLYP/cc-pVDZ	$0.644 \times \Delta E + 12.284$: no β-carbon $0.644 \times \Delta E + 11.140$: *one* β-carbon position $0.644 \times \Delta E + 10.150$: at least *two* β-carbon positions
	ΔE at AM1	$0.393 \times \Delta E_a + 17.600$: no β-carbon $0.393 \times \Delta E_a + 16.447$: *one* β-carbon position $0.393 \times \Delta E_a + 15.280$: at least *two* β-carbon positions
	$\Delta V_r^\ddagger = 6.84$ kcal/mol[a]	
$k_r(T)$ (ref 30)	$k_r = 1.06 \times 10^{-12} \times (T/298K)^{2.00} \times \exp(-860(\mathrm{cal/mol})/RT)$, $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$	

[a] Calculated value for reaction R_2 at the BH&HLYP/cc-pVDZ level of theory.

of 0.35, and the factor for reactions in group II can be assigned an average value of 0.15. Below is the summary for the partition function factors:

$$f_Q = 0.35 \quad \text{for reaction that yields product having no } \beta\text{-carbon OR reaction at a primary carbon site with product having one } \beta\text{-carbon} \tag{11a}$$

$$f_Q = 0.15 \quad \text{for other cases} \tag{11b}$$

As seen in Figure 4, there are two exceptions to the above analysis, namely, reactions R_4 and R_8 whose products have no β-carbon. These two cases are discussed separately at the end of the hindered rotation subsection below.

Hindered Rotations. For this reaction class, there are two kinds of internal rotors, namely, rotation of the OH group along C−O bond at the transition state and rotation of the alkyl group such as CH_3 along the C−C bond at both the transition states and the reactant alkanes, that need to be treated as hindered rotations. We used the approach proposed by Ayala et al.[29] for treating hindered rotations. Note that the reference reaction R_2 has both the OH and CH_3 internal rotations. Thus, the reaction class factor due to these hindered rotations is a measure of the substituent effects on the rate constant from these hindered rotors relative to that of the reference R_2 reaction. From our previous study of the CH_3 + alkanes hydrogen abstraction reaction class, the reaction class factor due to the rotation of the alkyl groups is close to unity and can be neglected.[39] In the present study, the reaction class factors due to the rotation of the CH_3 group for several reactions in the training set are plotted in Figure 5. Confirming our previous finding, these factors are close to unity, with a maximum deviation of about 20% over the temperature range 300−3000 K, and show a weak temperature dependence. For simplicity, we neglect its contribution to the reaction class factor.

The contribution from the OH hindered rotation to the reaction class factor is more noticeable. We found that for reactions at a primary carbon site of normal alkanes the correction factor is insensitive to the temperature and can be approximated as a constant:

$$f^{\mathrm{HR}} = 1.60 \tag{12a}$$

For other cases, the hindered rotation correction factor is temperature dependent. The average values were obtained and can be represented by the following expression:

$$f^{\mathrm{HR}} = 0.0390 \times 0.9998^{T} \times T^{0.6338} \qquad (12b)$$

These two expressions are plotted in Figure 6.

As mentioned above, reactions R_4 and R_8 show large deviations in the partition factor seen in Figure 4. They also have large deviations from others in the hindered rotor correction factor. One option is to treat these reactions explicitly. For simplicity, we can group these two reactions into group I (eq 11a). The partition factor would underestimate their rate constants by a factor of 3.5 and 5.5, respectively, at 300 K. However, the hindered rotation correction overestimates the total rate by a factor of 2 and 4 for reactions R_4 and R_8, respectively. Cancellation of errors from these two terms leads to a smaller and acceptable error factor of 1.5 at 300 K for both reactions.

RC-TST/LER Calculations of Rate Constants. What we have established so far are the necessary parameters, namely, symmetry number factor, tunneling factor, partition function factor, correction factor for hindered rotations, and potential energy factor, for application of the RC-TST theory to predict rate constants for any reaction in the OH + alkane class. By combining it 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 either the BH&HLYP/cc-pVDZ or AM1 level of theory. The procedure for calculating rate constants of an arbitrary reaction in this class is the following: (i) Calculate the potential energy factor using eq 6 with a $\Delta V_{\mathrm{r}}^{\ddagger}$ value of 6.84 kcal/mol. The reaction barrier height can be obtained using eqs 8a−c for BH&HLYP/cc-pVDZ reaction energies or eqs 9a−c for AM1 reaction energies. (ii) Calculate the symmetry number factor from eq 3 or see Table 1. (iii) Compute the tunneling factor using eq 10a, 10b, or 10c for primary, secondary, or tertiary carbon sites, respectively. (iv) Evaluate the partition function factor using eq 11a or 11b with the correction factor for OH hindered rotation using eq 12a or 12b. (v) The rate constants of the arbitrary reaction can be calculated by taking the product of the reference reaction rate constant given by eq 7 with the reaction class factors above. Table 3 summarizes the RC-TST parameters for this reaction class.

To illustrate the theory, we selected several reactions whose rate constants have been determined experimentally or derived from other experimental data or from theoretical calculations for more detailed discussion. In particular, we discuss the rate constants for reactions R_3−R_8 and the total rate constants for reactions between OH with propane, butane, and isobutane. Because there are no significant differences between rate constants calculated using the AM1 reaction energies and those using BH&HLYP/cc-pVDZ reaction energies, only the rate constants using the BH&HLYP reaction energies were used in this analysis.

Parts a−c of Figure 7 show the Arrhenius plots of the calculated rate constants using the RC-TST/LER method for the hydrogen abstraction reaction of propane at primary and secondary carbon sites and overall reaction at both sites, respectively. In the figures, the “RC-TST exact” notation means that the reaction class factors were calculated explicitly within the TST/Eckart framework rather than using the approximate expressions listed in Table 3. The RC-TST/LER rate constants for the reaction at the primary carbon agree very well with available data in the literature,[36,40−42] particularly within 6 and 20% of the experimental data from Droege et al.[42] at 300 and 600 K, respectively. For the abstraction at the secondary carbon (R_4), due to the deviations in the approximations of the partition function and hindered rotation factors discussed above, larger errors in the estimated rate constants are expected. In fact, the RC-TST/LER rate constant for this site underestimates the experimental data[42] by a factor of 2.5 at 300 K. However, as the temperature increases, the difference between the RC-TST/LER and experimental data decreases; for example, the difference is around 30% at 600 K. It is important to point out that the RC-TST exact rate constants are in excellent agreement with literature data.[36,41−44] This fact confirms that the TST/Eckart method provides an accurate framework for extrapolating the rate constants of a reference reaction to that of any reaction in the class. Furthermore, the relatively small differences between RC-TST exact and RC-TST/LER also indicate that approximations introduced in the RC-TST/LER method are reasonable. The overall rate constants for hydrogen abstraction of propane

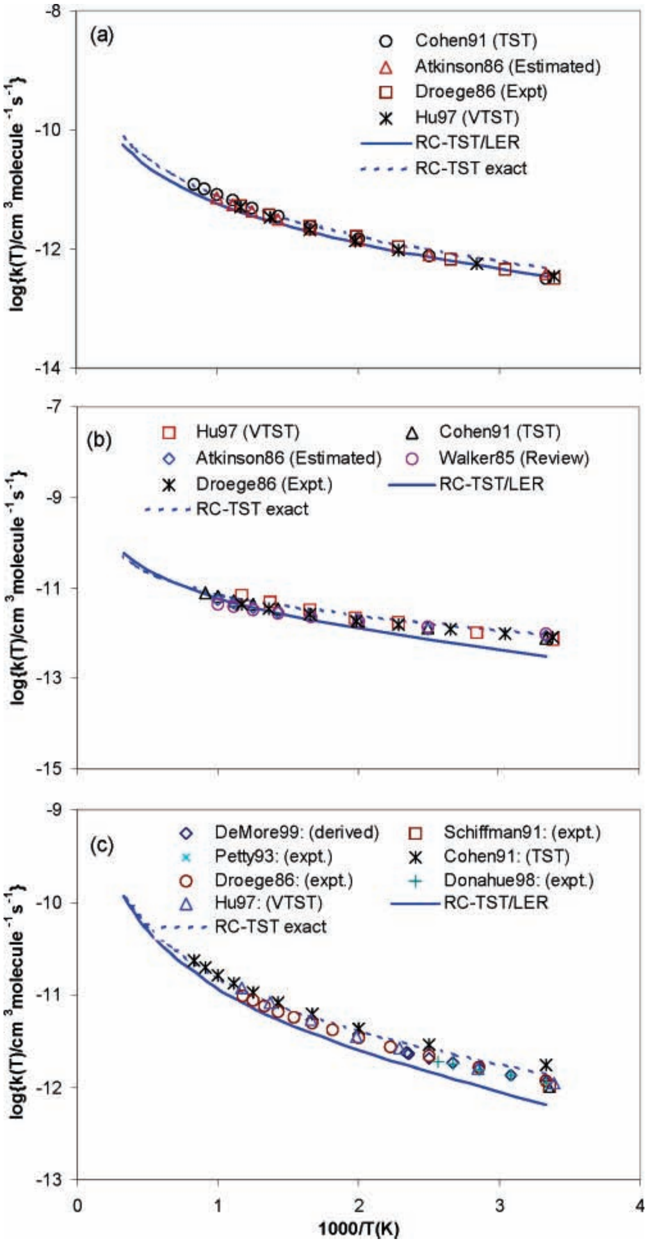

Figure 7. Arrhenius plots of the calculated rate constants along with literature values for the OH + C_3H_8 reaction: (a) for abstraction at the primary carbon site; (b) for abstraction at the secondary carbon sites; (c) for the total rate.

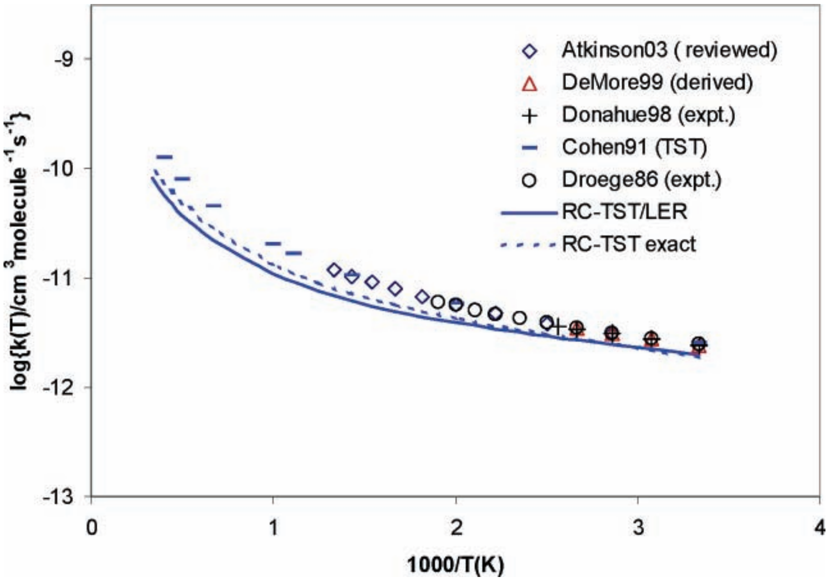

Figure 8. Arrhenius plots of the calculated total rate constants along with literature values for the OH + *n*-butane → H_2O + butyl reaction.

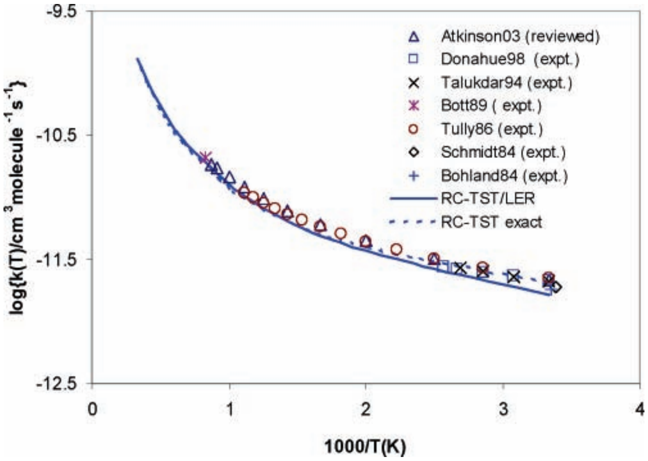

Figure 9. Arrhenius plots of the calculated total rate constants along with literature values for the OH + isobutane reaction.

by an OH radical are also in good agreement with available data in the literature.[36,42,43,45−48]

Figure 8 shows the Arrhenius plot for the total rate constants of the OH + *n*-butane reaction (R_5 + R_6). It is observed that the calculated values are within 18% of the experimental data in the temperature range 300−500 K.[43,45,48−50] In a higher temperature range where there is no direct experimental data, the calculated RC-TST/LER values are closed to the suggested data from Atkinson and Cohen with the largest error of a factor of 2 at 2500 K.

The rate constants for the reaction of OH with isobutane to form water and other products (R_7 + R_8) are plotted in Figure 9. Both the RC-TST exact and RC-TST/LER results nearly overlap with the available data in the literature.[48,49,51−55] The deviation is within 27% over the temperature range of literature data.

A more systematic analysis on the efficiency of the RC-TST method would be to compare the RC-TST/LER results with explicit theoretical calculations. As mentioned in our previous studies,[15,16] the RC-TST/LER methodology can be thought of as a procedure for extrapolating rate constants of the reference reaction to those of any given reaction in the class. Comparisons between the calculated rate constants for a small number of reactions using both the RC-TST/LER and full TST/Eckart methods would provide additional information on the accuracy of the RC-TST/LER method. To be consistent, the TST/Eckart rate constants of the reference reaction were used in calculation of TST/LER rate constants for this particular analysis rather than using the expression in eq 7. The results for this error analysis for 17 representative reactions (i.e., the comparisons between the RC-TST/LER and full TST/Eckart methods) are shown in Figure 10. Here, we plotted the absolute deviation defined by $|k^{\mathrm{TST/Eckart}} - k^{\mathrm{RC\text{-}TST/LER}}|/k^{\mathrm{TST/Eckart}}$ as a percent versus the temperature for 17 selected reactions. The relative errors are less than 100% for all reactions with only one exception of reaction R_{11} at 300 K. At higher temperature, the error for this reaction drops tremendously. This is certainly an acceptable level of accuracy for reaction engineering purposes. For most of the reactions in the training set, 14 out of 17 reactions, the absolute relative errors are within 40%; thus, it can be concluded that that the RC-TST can generally estimate thermal rate constants for reactions in this class within 40% when compared to those calculated explicitly using the TST/Eckart method.

Finally, we examined the systematic errors in different factors in the RC-TST/LER methods. The total error is affected by the errors in the approximations in the tunneling factor, the partition function factor, and the potential energy factor introduced in the method. It is noted that the symmetry number factor is “exact” and the error for the partition function factor does include the error in the approximation for the hindered rotation treatment. The deviations/errors between the approximated and exact factors are calculated at each temperature for every reaction in the training set and then averaged over the whole class. The error in the potential energy factor comes from the use of an LER expression as in eqs 8a−c or 9a−c; that of the tunneling factor, from using the three equations 10a−c; and that of the partition function factor, from using eqs 11a or 11b and eqs 12a or 12b. The results of the analysis on the errors from different relative rate factors, namely, f_κ, f_Q, and f_V, used in the RC-TST/LER method are shown in Figure 11. In this figure, we plotted the absolute errors averaged over all 17 reactions as a function of temperature. Of the three factors, errors from the partition function factor are the largest, followed by those of the potential energy factor. Errors from all components are less than 22%. The errors in tunneling factors and potential energy tend to decrease when the temperature increases, while the errors in the partition function factor have a minimum at 600 K. The

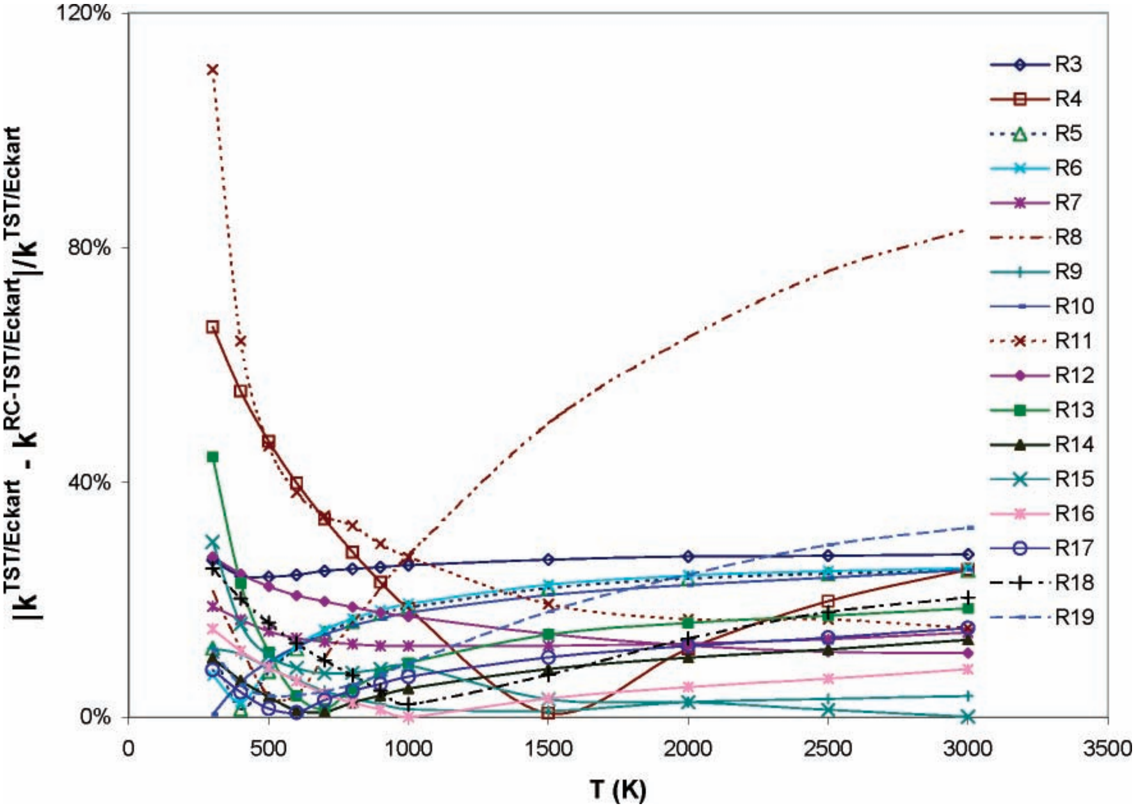

Figure 10. Relative absolute percent deviations as a function of temperature between rate constants calculated from the RC-TST/LER and full TST/Eckart methods for all selected reactions.

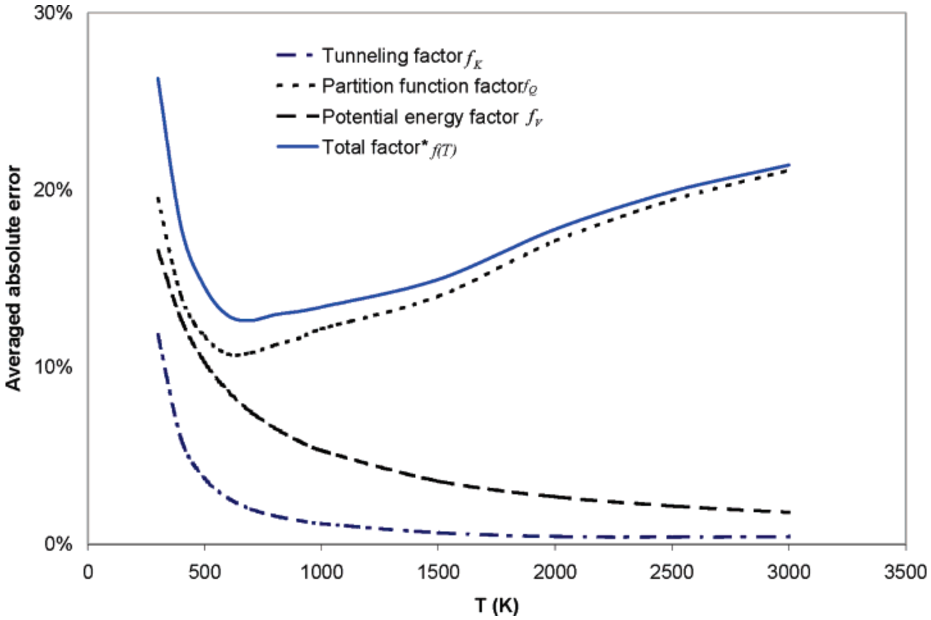

Figure 11. Averaged absolute errors of the total relative rate factors, $f(T)$ (eq 2), and its components, namely, the tunneling (f_K), partition function (f_Q), and potential energy (f_V) factors as a function of temperature.

total systematic errors due to the use of simple analytical expressions for different reaction class factors are less than 30% for the temperature range from 300 to 3000 K.

4. Conclusion

We have presented an application of the reaction class transition state theory in conjunction with the linear energy relationship (RC-TST/LER) for prediction of thermal rate constants of the OH + alkane → H_2O + alkyl reaction class. The RC-TST/LER method is shown to be both simple and effective for rate constant prediction for any reaction in a given class from only the reaction energy that can be calculated at either the BH&HLYP or AM1 level of theory. We have derived all parameters for the RC-TST/LER method for the above reaction class from rate constants of 19 representative reactions. We found that the estimated rate constants are in good agreement with available data in the literature. Detailed error analyses show that the systematic errors in the calculated rate constants arising from approximations used in the RC-TST/LER method are often less than 50% over the temperature range from 300 to 3000 K.

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