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Application of the reaction class transition state theory to the kinetics of hydrogen abstraction reactions of alkanes by atomic chlorine

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ABSTRACT

Kinetics of the hydrogen abstraction reaction of the class alkane + Cl → alkyl + HCl was studied using reaction class transition state theory (RC-TST) combined with linear energy relationships (LERs). The thermal rate coefficients for the reference reaction of ethane + Cl → ethyl + HCl, calculated by the micro-canonical variational transition state theory (μVT) incorporating small curvature tunneling (SCT), were taken from the literature. All necessary parameters were derived from density functional theory (DFT) calculations for a representative set of 29 reactions involving a range of hydrocarbons. Direct comparison to available experimental data reveals that the RC-TST/LER can predict rate coefficients for any reaction in the reaction class with acceptable accuracy. For the two test reactions outside of the representative set, our derived rate coefficients were in reasonable agreement with available data. Furthermore, our analyses indicate that RC-TST/LER gave systematic errors of less than 25% when compared to TST with one-dimensional Eckart tunneling approximation rate coefficients.

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1. Introduction

Hydrogen abstraction reactions involving alkanes and atomic chlorine (Cl) are a significant class of reactions in atmospheric chemistry and combustion chemistry. More than 60 theoretical and experimental studies for the reaction $CH_4 + Cl \rightarrow HCl + CH_3$ have been published and about 40 theoretical and experimental studies have appeared for the reaction $C_2H_6 + Cl \rightarrow HCl + C_2H_5$ [1]. The fate of Cl is not well-characterized since the rate coefficients for its reactions with many hydrocarbons, including alkanes, are not completely understood. These reactions are the major removal process for alkanes and other hydrocarbons in the global tropo-sphere and marine boundary layer [2]. Despite their importance, there are only 13 such elementary reactions of alkane + Cl for which some direct experimental measurements of kinetic data are available, and these are available only over limited temperature ranges. Of these 13 reactions, only three reactions have been studied more than twice, and for four reactions, rate coefficients only at room temperature are reported. Experimental difficulties include secondary reactions of the intermediate alkyl radicals and instru-mental limitations for wide temperature ranges. To construct the global detailed kinetic mechanisms for all possible reactions, rate coefficients of all of the reactions in the class are needed. Recently, first-principles based theoretical calculations are providing an alternative route to the necessary kinetic information for hydrogen abstractions by Cl [3–5].

Rate coefficients for a large number of reactions in a given class can be estimated using the reaction class transition state theory with linear energy relationship (RC-TST/LER) method. The RC-TST/LER theory provides a cost-effective approach to estimating the thermal rate coefficients of all arbitrary reactions in the given class under the transition state theory framework. The central principle of RC-TST is that all reactions in the same class have the same reactive moiety in-volved in bond changes during the reaction, and thus are expected to have similar features on their potential surfaces along the specific reaction pathway. Rate coefficients of any reaction in the given class can be determined by the extrapolation from that of a reference reaction with a relative rate scaling factor expression that applies to the whole class. Moreover, within a given reaction class there is a linear energy relationship (LER) between the classical barrier heights and reaction energies [6–8]. By combining the basics of RC-TST with LER, thermal rate coefficients for any reaction in the class can be predicted from just its reaction energy once all reaction class parameters are determined. The definitions of these parame-ters are given in Section 2.1. Within the RC-TST/LER method the reaction energy can be simply obtained at a relatively low level of theory, e.g., AM1. Although AM1 is a low level of theory, it has proven to be very practical when combined with RC-TST/LER. Thus the use

of AM1 makes RC-TST/LER a cost effective method for predicting thermal rate coefficients. Successful applications of RC-TST/LER have been demonstrated by a large number of studies in various systems [6,9–11].

The purpose of this study is to provide first-principles based kinetics information for hydrogen abstraction from various alkanes by Cl. The aim is to determine reaction class parameters for the alkane + Cl system. To do so, a representative set of hydrogen abstractions by Cl from alkanes at different positions in this class was selected and then explicit rate calculations by TST were performed. Finally, all reaction class parameters were determined by deriving correlated factors for the rate coefficients of reactions in the representative set of the class relative to the chosen reference reaction, for which highly accurate rate coefficients are derived from either experiment or theoretical calculation. To determine RC-TST/LER parameters for alkane + Cl class, 29 reactions involving 13 different alkanes are considered as a representative set. These reactions are shown below:

alkane + Cl	→ HCl + alkyl		
C_2H_6 + Cl	→ HCl + $CH_3\underline{C}H_2$	(R01)	p
C_3H_8 + Cl	→HCl + $CH_3CH_2\underline{C}H_2$	(R02)	p
	→ HCl + $CH_3\underline{C}HCH_3$	(R03)	s
n-C_4H_{10} + Cl	→ HCl + $CH_3(CH_2)_2\underline{C}H_2$	(R04)	p
	→ HCl + $CH_3CH_2\underline{C}HCH_3$	(R05)	s
iso-C_4H_{10} + Cl	→ HCl + $CH_3CH(CH_3)\underline{C}H_2$	(R06)	p
	→ HCl + $CH_3\underline{C}(CH_3)CH_3$	(R07)	t
n-C_5H_{12} + Cl	→ HCl + $CH_3(CH_2)_3\underline{C}H_2$	(R08)	p
	→ HCl + $CH_3(CH_2)_2\underline{C}HCH_3$	(R09)	s
	→ HCl + $CH_3CH_2\underline{C}HCH_2CH_3$	(R10)	s
iso-C_5H_{12} + Cl	→ HCl + $\underline{C}H_2CH(CH_3)CH_2CH_3$	(R11)	p
	→ HCl + $CH_3CH(CH_3)CH_2\underline{C}H_2$	(R12)	p
	→ HCl + $CH_3CH(CH_3)\underline{C}HCH_3$	(R13)	s
	→ HCl + $CH_3\underline{C}(CH_3) CH_2CH_3$	(R14)	t
neo-C_5H_{12} + Cl	→ HCl + $CH_3C(CH_3)_2\underline{C}H_2$	(R15)	p
n-C_6H_{14} + Cl	→ HCl + $CH_3(CH_2)_4\underline{C}H_2$	(R16)	p
	→ HCl + $CH_3(CH_2)_3\underline{C}HCH_3$	(R17)	s
	→ HCl + $CH_3(CH_2)_3\underline{C}H CH_2CH_3$	(R18)	s
iso-C_6H_{14} + Cl	→ HCl + $\underline{C}H_2CH(CH_3)(CH_2)_2CH_3$	(R19)	p
	→ HCl + $CH_3CH(CH_3)(CH_2)_2\underline{C}H_2$	(R20)	p
	→ HCl + $CH_3CH(CH_3)CH_2\underline{C}HCH_3$	(R21)	s
	→ HCl + $CH_3CH(CH_3)\underline{C}HCH_2CH_3$	(R22)	s
$CH_3CH_2CH(CH_3)CH_2CH_3$ + Cl	→ HCl + $CH_3CH_2CH(CH_3)CH_2\underline{C}H_2$	(R23)	s
	→ HCl + $CH_3CH_2CH(CH_3)\underline{C}HCH_3$	(R24)	s
	→ HCl + $CH_3CH_2CH(\underline{C}H_2)CH_2CH_3$	(R25)	p
$CH_3CH(CH_3)CH(CH_3)CH_3$ + Cl	→ HCl + $CH_3CH(CH_3)CH(\underline{C}H_2)CH_3$	(R26)	p
neo-C_6H_{14} + Cl	→ HCl + $\underline{C}H_2C(CH_3)_2CH_2CH_3$	(R27)	p
	→ HCl + $CH_3C(CH_3)_2CH_2\underline{C}H_2$	(R28)	s
	→ HCl + $CH_3C(CH_3)_2\underline{C}HCH_3$	(R29)	p

where the underlined carbon atom, $\underline{C}$, contains the radical site in the products of hydrogen abstraction reactions. Of these 29 reactions, 16 reactions represent hydrogen abstractions from the primary carbons (p), 11 reactions represent hydrogen abstractions from the secondary carbons (s) and two reactions represent hydrogen abstractions from the tertiary carbons (t).

2. Methodology and computational details

2.1. Reaction class transition state theory (RC-TST)

Since details of the RC-TST/LER method has been given in detail in previous reports [6,7], we focus on the necessary parameters here. Within the RC-TST framework, the rate coefficient of an arbitrary reaction (denoted as R_a) in a given reaction class, $k_a(T)$, is proportional to the rate coefficient of the reference reaction (denoted as R_r) of the class, $k_r(T)$. The proportionality function, $f(T)$ is a temperature-dependent relative rate function.

$$k_a(T) = f(T)k_r(T) \tag{1}$$

For the reference reaction, one generally selects the smallest reaction (having the least number of atoms) in which it can represent the behaviors of chemical moiety for the whole class.

Moreover, rate coefficients of the smallest reaction can be calculated accurately from first principles using high level of theory. The key approach of the RC-TST method is to factor $f(T)$ into different components:

$$f(T) = f_\kappa(T)f_\sigma f_Q(T)f_V(T)f_{HR}(T) \tag{2}$$

where $f_\kappa, f_\sigma, f_Q, f_V$ and f_{HR} are tunneling, symmetry number, partition function, potential energy and hindered rotor factors, respectively. These factors are simply the ratio of the corresponding components in the well-known TST expression for the two reactions:

$$f_\kappa(T) = \frac{\kappa_a(T)}{\kappa_r(T)} \tag{3}$$

$$f_\sigma = \frac{\sigma_a}{\sigma_r} \tag{4}$$

$$f_Q(T) = \left(\frac{Q_a^{\neq}(T)}{\Phi_a^R(T)}\right) \bigg/ \left(\frac{Q_r^{\neq}(T)}{\Phi_r^R(T)}\right) = \left(\frac{Q_a^{\neq}(T)}{Q_r^{\neq}(T)}\right) \bigg/ \left(\frac{\Phi_a^R(T)}{\Phi_r^R(T)}\right) \tag{5}$$

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

$$f_{HR}(T) = \frac{HR_a(T)}{HR_r(T)} \tag{7}$$

where $\kappa(T)$ is the transmission coefficient accounting for the quantum mechanical tunneling effects, σ is the reaction symmetry number, $Q^{\neq}$ and Φ^R are the total partition functions (per unit volume) of the transition state and reactants, respectively, $\Delta V^{\neq}$ is the classical barrier height, HR symbolized the total partition function due to the hindered rotor approximation, T is the temperature in Kelvin, and k_B is the Boltzmann constant.

The important task is to derive general expressions for these factors linking the rate coefficients of R_r and those of R_a in the same class without having to calculate $k_a(T)$ explicitly. This is done by performing explicit rate determinations for the above representative set of reactions using the TST with the one-dimensional Eckart tunneling approximation [12,13] (TST/Eckart) then analyzing the 'exact' calculated relative rate factors as functions of temperature to derive general expressions for the whole class. The rationale for using the TST/Eckart method for this purpose has been discussed previously [6,7,9]. The calculated barrier heights and reaction energies for the above representative set of reactions also allow us to determine the LER between them that also can be used for the entire class.

Comparisons of rate coefficients derived from our RC-TST/LER parameters with available experimental data from the literatures and from our explicit TST/Eckart for R01–R29 reactions are presented. In addition, our RC-TST/LER parameters are further applied to estimate thermal rate coefficients for two test cases outside of the representative set. Validation of these two test cases will be analyzed and discussed.

2.2. Electronic structure calculations

All the electronic structure calculations were performed using the Gaussian 03 suite of program [14]. The geometries and harmonic vibrational frequencies of all the stationary points for all reactions in the given class (the reactants, transition state, and products) were calculated at the hybrid BH&HLYP level of density functional theory with the cc-pVDZ basis set. The BH&HLYP method was found previously to be sufficiently accurate for predicting the transition state properties for hydrogen abstraction reactions by a radical [15–17]. For the reference reaction, rate coefficients calculated at the microcanonical variational transition state theory (μVT) augmented with

the multi-dimensional semiclassical small curvature tunneling (SCT) method from Fernández-Ramos et al. [18] were adopted. To obtain the RC-TST/LER parameters as described in Section 2.1, rate coefficients of all reactions in the above representative reaction set were calculated employing the TST/Eckart method. The hindered rotor factor using the method of Ayala and Schlegel [19] was included explicitly in the rate coefficients of all reactions. The thermal rate coefficients at the TST/Eckart were calculated using TheRate program [17] for the temperature range from 200 to 1000 K, which is sufficient for many atmospheric reactions.

3. Results and discussion

3.1. Rate coefficients of the reference reaction

The first task of applying RC-TST to any reaction in the given class is to determine the rate coefficients of the reference reaction as accurately as possible. The rate coefficients can either be obtained from experimental data or calculated from first principles. In addition, choosing the reference reaction for the RC-TST/LER is not limited to just the smallest reaction, as long as the chosen reaction can represent the reaction moiety of the whole class, it can be an excellent choice. Previous studies by Ratkiewicz [19,20] showed the validity of RC-TST using the first principle rate coefficient from other groups; however, the smallest reaction was still selected as the referent reaction. In this study, the CH$_4$ + Cl reaction, symbolized as R00, excluded from our reaction class, was not chosen as the reference reaction. Although the reaction of methane and Cl is the smallest reaction, its unique dynamic behaviors are different from larger hydrocarbons due to its lack of a C–C bond. For instance, R00 lacks the C–C vibrational mode and the hindered rotor motion. In our study, R00 showed its unique behavior with a higher barrier height than others in our reaction class: 12.3 kcal mol^{-1} for R00 versus about 0.5–6.5 kcal mol^{-1} for other reactions in the reaction class. In addition, our study of thermal rate coefficients utilizing the RC-TST/Eckart/HR method showed that rate coefficients for R00 are very small compared to other reactions in our reaction class (see Fig. S1 in the Supporting material). The previous study of another reaction class has also shown that reaction of methane is not a good representative reaction to be used as the reference reaction for other hydrocarbons in the class [9]. In fact, our analysis on thermal rate coefficients of ethane confirms this fact by showing that the thermal rate coefficients of ethane reaction with Cl denoted R01 have values in the same range as other reactions in the class (see Fig. S1 in the Supporting material). For these reasons, the parameters for the RC-TST/LER are derived by the use of the reaction of Cl with ethane (R01) as the reference reaction.

The rate coefficients of the reference reaction reported by Fernández-Ramos et al. [18], calculated from direct ab initio dynamics methods based on the μVT/SCT methods, were adopted. In their study, static electronic calculations are achieved by the Møller–Plesset perturbation theory with the augmented correlation-consistent double-zeta basis set (MP2/aug-cc-pVDZ). It is well-known that μVT/SCT method is much more accurate for predicting thermal rate coefficients than the classical TST/Eckart method. Rate coefficients from Fernández-Ramos et al. [18] coefficients are fitted to an Arrhenius expression which is given by:

$$k_r(T) = 4.70 \times 10^{-13} T^{0.79} e^{110.7/T} \quad (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) \tag{8}$$

The rate coefficients for reference reaction R01 from Fernández-Ramos et al. [18] are shown in Table 1. And the comparison between these rate coefficients with available experimental values shows excellent agreement as displayed in Fig. 1. Therefore, rate coefficients of R01 from Fernández-Ramos et al. [18] will be used in our RC-TST/LER study without any further modification.

Table 1
Thermal rate coefficients $k(T)$ (cm^3 molecules^{-1} s^{-1}) calculated at the microcanonical variational transition state theory with small curvature tunneling method (μVT/SCT) for the reference reaction, C$_2$H$_6$ + Cl → HCl + C$_2$H$_5$ reaction, or R01.

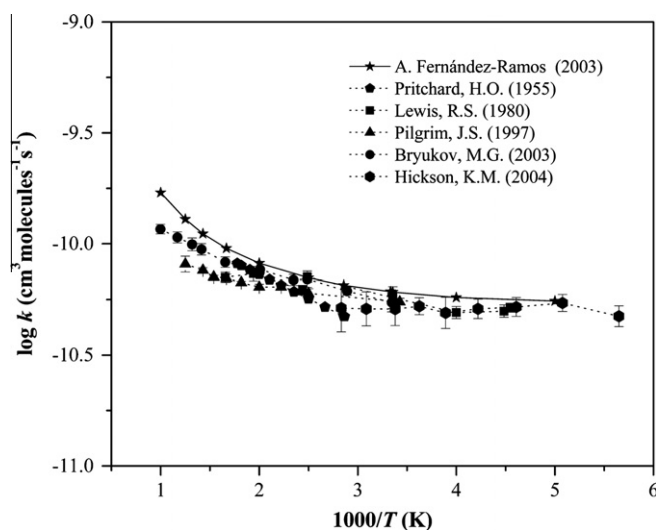| Temperature (K)	$k_r(T)^{\mu VT/SCT}$ (cm^3 molecules^{-1} s^{-1})
200	5.54×10^{-11}
250	5.75×10^{-11}
298	6.08×10^{-11}
300	6.11×10^{-11}
350	6.52×10^{-11}
400	7.03×10^{-11}
500	8.18×10^{-11}
600	9.54×10^{-11}
700	1.11×10^{-10}
800	1.29×10^{-10}
1000	1.70×10^{-10}

Fig. 1. Arrhenius plots of rate coefficients calculated by Fernández-Ramos [18] and available experimental data rate coefficients for the reference reaction R01.

3.2. Thermal rate coefficients for arbitrary reaction

Fig. 2 displays the calculated rate coefficients for arbitrary reactions R02–R29 utilizing the RC-TST/LER method. It can be seen that rate coefficients increase with increasing temperature. Moreover, values of rate coefficients seem likely to be grouped based on the type of carbon atom from which the H-atom is abstracted, dashed line for primary carbon, solid line for secondary carbon and dotted line for tertiary carbon. This suggests that a similar chemical moiety is involved in each of the abstraction groups. However, there is one reaction (R25) whose rate coefficients are quite different from those of other reactions in the representative reaction set. The reaction class parameters in the next section will be derived based on the three groups of hydrogen abstractions from primary, secondary and tertiary carbon atom.

3.3. Reaction class parameters

This section describes how each factor of the RC-TST/LER was derived using the representative reaction set.

3.3.1. Linear energy relationship

In a previous study by Zhang and Truong [6] and also from our previous report [9], it was found that within a given reaction class there is a linear energy relationship between the reaction barriers and reaction energies identical to the Evans–Polanyi linear energy relationship [21] which assumes the difference in activation energy
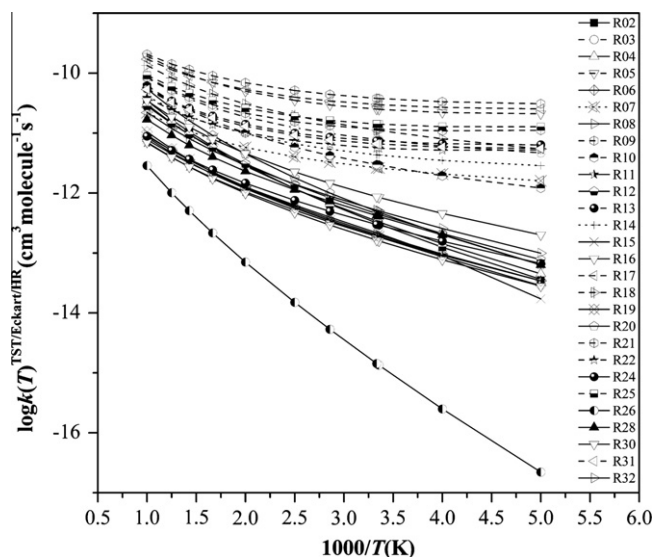
Fig. 2. Arrhenius plot of the calculated TST/Eckart/HR thermal rate coefficients for arbitrary reactions.

(reaction barrier height) between two reactions of the same family is proportional to the difference of their enthalpy of reaction (reaction energy). These reaction energies can be calculated at a lower level of theory such as AM1 [22]. Our aim here is to obtain the relationship between the barrier height and the reaction energy so that

one only needs the reaction energy calculated by a relatively simple method to predict the thermal rate coefficient for a given reaction in the class without further calculations of the transition state geometry, energy and frequencies. In a previous study by Truong et al. [8], it was found that within the reaction class framework, accurate relative barrier heights can be obtained from a reasonably low level of theory such as DFT. To also illustrate this point here, we provide the relative barrier heights (listed in Table 2) calculated at the IMOMO(CCSD(T)/cc-pVTZ//BH&HLYP/cc-pVDZ) level, where the principal reaction is used as the model system, and at the BH&HLYP/cc-pVDZ level. The IMOMO method is employed in combination with the reaction class concept to give rather accurate absolute classical barrier heights [23]. The relative barrier heights are also shown in Table 2. For the principal reaction, the reaction barrier height calculated at BH&HLYP/cc-pVDZ is corrected to the reaction barrier height calculated at CCSD(T)/cc-pVTZ level. The data for all reactions, including primary, secondary, and tertiary hydrogen abstraction reactions were fitted to the following relationships.

$$\Delta V^{\neq} = 0.6244\Delta E$$
$$+ 17.261 \ (\text{kcal mol}^{-1}) \quad (\Delta E \text{ from AM1 calculations}) \tag{9a}$$

$$\Delta V^{\neq} = 0.9773\Delta E$$
$$- 1.1786 \ (\text{kcal mol}^{-1}) \quad (\Delta E \text{ from BH&HLYP calculations}) \tag{9b}$$

Table 2
Reaction barriers ($\Delta V^{\neq}$), reaction energies (ΔE) and deviations (kcal mol^{-1}).

Reaction	ΔE		$\Delta V^{\neq}$		$\Delta V^{\neq}_{LER}$ [d]	$|\Delta V^{\neq} - \Delta V^{\neq}_{LER}|$ [e]
	DFT[a]	AM1[b]	DFT[a]	DFT[c]		
R01	5.74	−20.70	7.53 (0.00)[f]	4.65 (0.00)[f]	4.34	0.31
R02	6.35	−19.68	7.57 (−0.04)	5.04 (−0.39)	4.97	0.07
R03	2.46	−25.96	3.63 (3.90)	0.69 (3.95)	1.05	0.35
R04	6.26	−19.70	7.38 (0.15)	4.93 (−0.28)	4.96	0.03
R05	2.68	−25.73	3.05 (4.47)	0.50 (4.15)	1.19	0.69
R06	6.27	−20.01	7.08 (0.45)	4.84 (−0.20)	4.77	0.08
R07	0.22	−27.97	0.53 (7.00)	1.21 (3.44)	0.15	1.06
R08	6.28	−19.69	7.28 (0.24)	4.87 (−0.22)	4.96	0.09
R09	2.63	−25.76	3.60 (3.92)	1.24 (3.41)	1.18	0.06
R10	2.87	−25.37	5.17 (2.36)	3.08 (1.57)	1.42	1.66[g]
R11	6.10	−20.09	6.98 (0.55)	4.80 (−0.15)	4.72	0.08
R12	5.33	−20.78	7.07 (0.46)	4.66 (−0.02)	4.29	0.38
R13	2.48	−25.33	2.71 (4.82)	0.49 (4.16)	1.45	0.95
R14	0.15	−27.56	0.71 (6.82)	1.61 (3.04)	0.41	1.20
R15	6.80	−19.22	6.81 (0.72)	4.91 (−0.26)	5.26	0.35
R16	6.27	−19.69	7.26 (0.27)	4.86 (−0.21)	4.96	0.10
R17	2.63	−25.75	3.50 (4.02)	1.18 (3.47)	1.18	0.00
R18	2.82	−25.40	4.84 (2.69)	2.92 (1.73)	1.40	1.52
R19	6.07	−20.10	6.92 (0.61)	4.80 (−0.15)	4.71	0.09
R20	6.27	−20.58	7.19 (0.34)	4.80 (−0.15)	4.41	0.39
R21	1.95	−25.95	3.20 (4.33)	0.96 (3.68)	1.06	0.10
R22	2.65	−25.11	4.00 (3.52)	2.15 (2.50)	1.58	0.57
R23	5.25	−20.84	6.95 (0.57)	4.59 (0.06)	4.25	0.34
R24	2.37	−25.48	2.50 (5.02)	0.46 (4.19)	1.35	0.89
R25	5.39	−21.41	9.82 (−2.29)	5.05 (−0.40)	4.25	0.80
R26	5.77	−19.92	6.67 (0.85)	4.56 (0.09)	4.82	0.27
R27	5.17	−20.22	6.75 (0.78)	4.41 (0.24)	4.64	0.23
R28	2.78	−25.22	2.33 (5.20)	0.49 (4.16)	1.51	1.02
R29	6.82	−19.19	6.60 (0.92)	4.84 (−0.19)	5.28	0.44
MAD						0.64[h]

[a] Calculated at BH&HLYP/cc-pVDZ level of theory.
[b] Calculated at AM1 level of theory.
[c] Calculated at the IMOMO(CCSD(T)/cc-pVDZ//BH&HLYP/cc-pVDZ) level of theory as described in the text.
[d] Calculated from LER using reaction energies calculated at AM1 level of theory; Eq. (9a).
[e] $\Delta V^{\neq}$ from IMOMO(CCSD(T)/cc-pVDZ//BH&HLYP/cc-cVDZ) calculations; $\Delta V^{\neq}_{LER}$ from the Linear Energy Relationship using BH&HLYP/cc-pVDZ and AM1 reaction energies.
[f] The numbers in the parentheses are the relative barrier heights.
[g] Max absolute deviation of all reactions R01−R29.
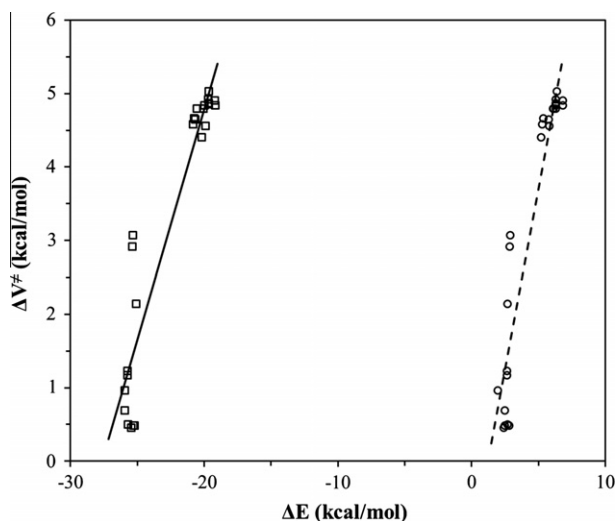[h] Mean absolute deviations for reactions R01−R29.

Fig. 3. Linear energy relationships (LERs) between reaction energy (ΔE) and reaction barrier height ($\Delta V^{\neq}$). ΔE's were calculated at the BH&HLYP/cc-pVDZ (circle symbols and dashed line) and AM1 level of theory (square symbols and solid line). Barrier heights were calculated at IMOMO(CCSD(T)/cc-pVDZ//BH&HLYP/cc-pVDZ) level of theory.

Fig. 4. Plot of partition function factors f_Q as functions of the temperature for R02–R29: primary carbon (solid line), secondary carbon (dashed line), and tertiary carbon (dotted line).

The standard deviations are 0.64 kcal mol^{-1} for expressions (9a) and (9b). Note that these LER relationships are universal to all reactions in the class and do not depend on a specific reaction chosen as the reference reaction in the RC-TST method. Fig. 3 shows the linear energy relationships between reaction barrier heights calculated at the IMOMO(CCSD(T)/cc-pVTZ//BH&HLYP/cc-pVDZ) level of theory and reaction energies calculated at BH&HLYP and AM1 levels of theory, respectively. The calculated reaction energies, reaction barrier heights and absolute deviations between calculated barrier heights from LER and those from full quantum calculation are listed in Table 2. It can be seen that absolute deviations for the reaction barrier height between LER and IMOMO(CCSD(T)/cc-pVTZ//BH&HLYP/cc-pVDZ) calculation are smaller than 1.0 kcal mol^{-1}. Note that BH&HLYP is able to predict the relative barrier heights as accurately as predicted with the IMOMO(CCSD(T)//BH&HLYP) level within 1.00 kcal mol^{-1} difference (differences of values in parentheses in columns 4 and 6 of Table 2) except for the R10, R18 and R28 reactions where the difference are 1.66, 1.52 and 1.02 kcal mol^{-1}, respectively.

The averaged deviation of reaction barrier heights predicted from AM1 reaction energy using LER is 0.64 kcal mol^{-1} for all reactions. Therefore, this LER approach can be used to estimate the relative barrier height quickly with an acceptable deviation.

3.3.2. Partition function factor

In previous study by Zhang and Truong [6], it was noted that f_Q results mainly from the difference in coupling between the substituents and the reactive moiety of the considered reaction and the reference reaction. In calculations of f_Q, vibrational frequencies calculated at the BH&HLYP/cc-pVDZ level were used. Also since the C$_2$H$_6$ + Cl reaction was used as the reference reaction, hindered rotor treatments for the methyl and ethyl groups were explicitly included in the reference rate coefficients. Fig. 4 shows the temperature dependence of f_Q for different types of hydrogen atom. f_Q varies narrowly from 0.0 to 1.2 and again for simplicity we approximate f_Q to be 0.7, 0.4, and 0.3 for primary, secondary and tertiary hydrogen respectively. These three values were chosen by averaging the f_Q from the representative set at 1000 K (primary, secondary and tertiary). This would make the largest errors in f_Q, which occur at low temperatures, range from about 1 to 3 for reactions R02, R07, R22,
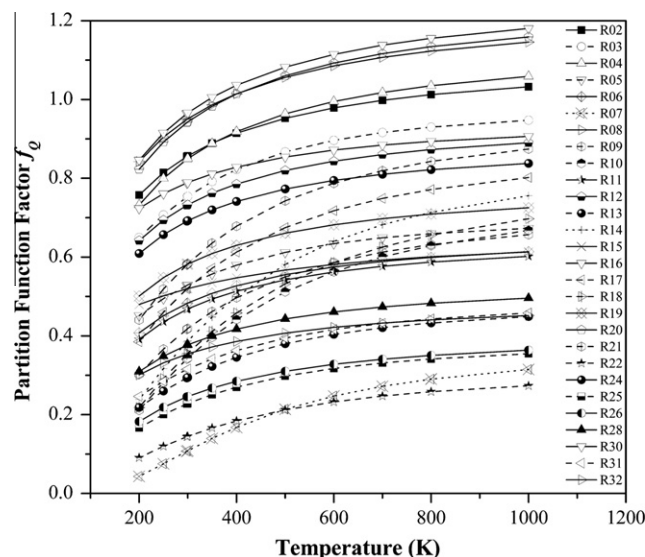
R24, R25, R26 and R29 with the exception of reaction R07, which has an error factor of 6. This is certainly an acceptable level of accuracy in kinetics modeling. One could further introduce the temperature dependence into f_Q at the lower temperature range; however, we found that it would only reduce the error in f_Q slightly.

3.3.3. Symmetry number factor

The symmetry number factors were simply derived from the ratio of symmetry numbers of arbitrary and principal reactions using R01 as the reference reaction.

3.3.4. Tunneling factor

We used the Eckart tunneling method [24] to calculate the tunneling factor, which is the ratio of tunneling coefficients for the arbitrary and reference reactions. This method requires only the imaginary frequency, forward and reverse barrier height of the reaction. Table 3 shows the calculated tunneling factors of reactions in the class using barrier heights calculated from the BH&HLYP level for R01 as the reference reaction. Since all reactions in the class are endothermic, the forward barriers heights dominate the quantum tunneling effect. At a given temperature, the f_κ values of the abstraction reactions for the same type of hydrogen atom are plotted in Fig. 5. For reaction R01 as the reference reaction, the fitted equations for abstraction of hydrogen from a primary, secondary and tertiary carbon are

$$F_\kappa(T) = 0.9738 - 0.9653 \\ \times \exp(-0.0079T) \quad \text{for primary carbon} \tag{10a}$$

$$F_\kappa(T) = 0.9836 - 2.4279 \\ \times \exp(-0.0093T) \quad \text{for secondary carbon} \tag{10b}$$

$$F_\kappa(T) = 0.8854 - 1.6290 \\ \times \exp(-0.0053T) \quad \text{for tertiary carbon, respectively.} \tag{10c}$$

3.3.5. Potential energy factor

The potential energy factor f_V can be calculated using Eq. (6), where $\Delta\Delta V^{\neq}$ is the difference in the classical reaction barriers of arbitrary reaction and reference reaction. The LERs discussed above

Table 3
Calculated symmetry number factors f_σ and tunneling factors $f_\kappa(T)$ at 298 K (using R01 as a reference reaction).

Reaction	f_σ	f_κ(298 K)
R01	1.000(6)[a]	1.000(2.261)[a]
R02	1.000	0.911
R03	0.333	0.862
R04	1.000	0.913
R05	0.667	0.841
R06	1.500	0.844
R07	0.167	0.473
R08	1.000	0.906
R09	0.667	0.852
R10	0.333	0.845
R11	1.000	0.836
R12	0.500	0.959
R13	0.333	0.816
R14	0.167	0.640
R15	2.000	0.781
R16	1.000	0.902
R18	0.667	0.773
R19	1.000	0.839
R20	0.500	0.896
R21	0.333	0.884
R22	0.333	0.853
R23	1.000	0.958
R24	0.667	0.856
R25	0.500	0.896
R26	2.000	0.900
R27	0.500	0.989
R28	0.333	0.802
R29	1.500	0.766

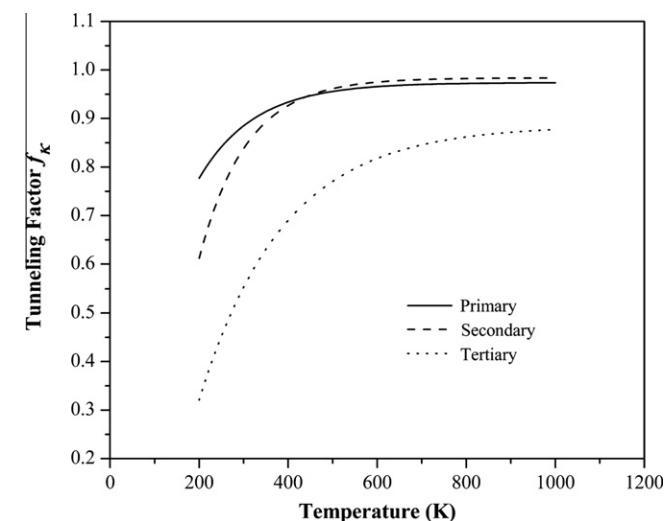[a] Values in parentheses are the symmetry and tunneling coefficient.

Fig. 5. Plot of tunneling factor f_κ as a function of temperature for hydrogen abstraction reactions at the primary carbon (solid line), secondary carbon (dash line) and tertiary carbon (dot line).

3.3.6. Hindered rotor factor

It is important to point out that the motion of the internal rotor of the methyl group in the reactive moiety is already treated explicitly in the rate coefficients of the reference C_2H_6 + Cl reaction. Here we examined the correction factor for internal rotors of the substituent groups. In this study, the hindered rotor factor was computed using the same method as in the work of Ayala and Schlegel [25]. The absolute hindered rotor factors for abstraction

Table 4
Calculated hindered rotor factors $f_{HR}(T)$ to the rate coefficient for abstraction of hydrogen from a primary, secondary and tertiary carbon.

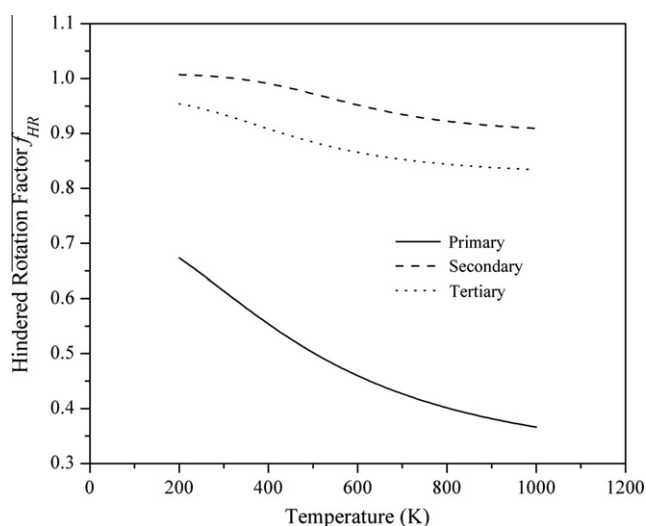| Temperature (K)	$f_{HR}(T)$		
	Primary	Secondary	Tertiary
200	0.672	1.005	0.955
250	0.646	1.005	0.944
298	0.616	1.004	0.934
300	0.615	1.004	0.934
350	0.582	0.998	0.922
400	0.553	0.990	0.909
500	0.501	0.971	0.885
600	0.460	0.951	0.866
700	0.428	0.935	0.852
800	0.402	0.923	0.842
1000	0.365	0.908	0.835

Fig. 6. Plot of hindered rotor factors versus the temperature for primary carbon (solid line), secondary carbon (dash line) and tertiary carbon (dot line).

Table 5
Ab initio derived parameters and formulation of the RC-TST/LER method for the alkane + Cl hydrogen abstraction reaction class.

	$k_a(T) = f_\kappa(T)f_\sigma f_Q f_V(T)k_r(T)HR(T)$
	$f_V(T) = \exp[-(\Delta V^\neq - \Delta V_r^\neq)/kBT]$
	C_2H_6 + Cl as the reference reaction
$f_\kappa(T)$	$0.9738 - 0.9653\exp(-0.0079T)$ for primary carbon
	$0.9836 - 2.4279\exp(-0.0093T)$ for secondary carbon
	$0.8854 - 1.6290\exp(-0.0053T)$ for tertiary carbon
f_Q	0.7 (primary), 0.4 (secondary), and 0.3 (tertiary)
$\Delta V^\neq$ (kcal mol^{-1})	$(0.9773\Delta E - 1.1786)$ for all types,
	ΔE at the BH&HLYP/cc-pVDZ level
	$(0.6244\Delta E + 17.261)$ for all types,
	ΔE at the AM1 level
$\Delta V_r^\neq$ (kcal mol^{-1})	7.526
$k_r(T)$	$4.70 \times 10^{-13} T^{0.79} e^{110.7/T}$ (cm^3 molecule^{-1} s^{-1})
$f_{HR}(T)$	$0.2886 + 0.4436/[1 + (\frac{T}{482.2})^{2.127}]$ for primary carbon
	$0.8987 + 0.1.93/[1 + (\frac{T}{591.8})^{4.276}]$ for secondary carbon
	$0.8223 + 0.1415/[1 + (\frac{T}{460.7})^{3.0987}]$ for tertiary carbon

of hydrogen from a primary, secondary and tertiary carbon are shown in Table 4 and plotted in Fig. 6. It can be seen from the Fig. 6 that the hindered rotor factors are dependent on the temperature. From Table 4, the ratios of the secondary and tertiary
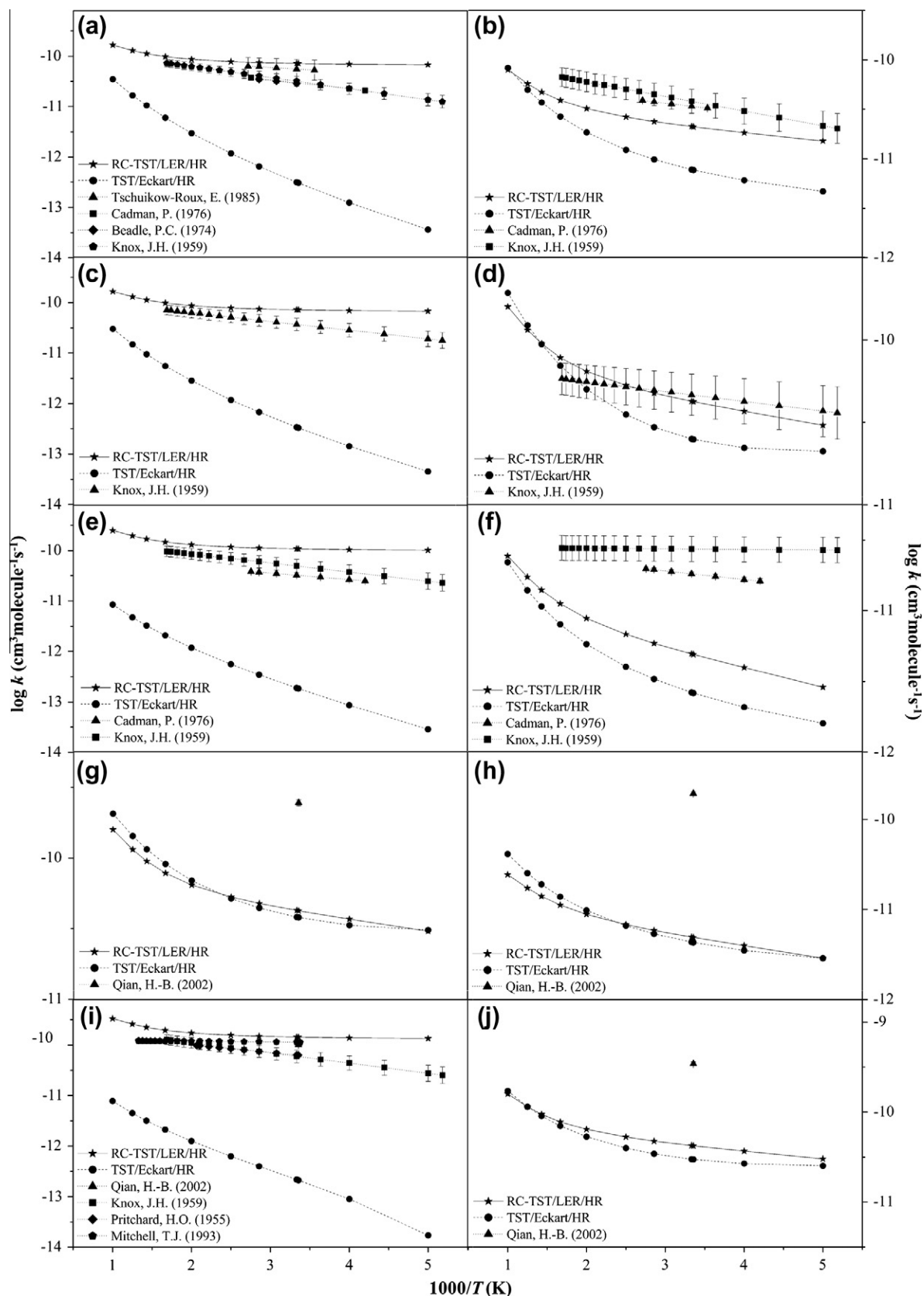
Fig. 7. Arrhenius plots of the calculated rate coefficients using the RC-TST/LER method for reaction R02 (a), R03 (b), R04 (c), R05 (d), R06 (e), R07 (f), R09 (g), R14 (h), R15 (i) and R17 (j) along with the available literature values as well as the calculated TST/Eckart/HR rate coefficients.

abstraction to primary abstraction indicate that the effects of $f_{HR}(T)$ due to the substituent groups are not small as these relative factors

are not close to unity for the entire temperature range. For this reason, hindered rotor corrections are still needed for more accurate
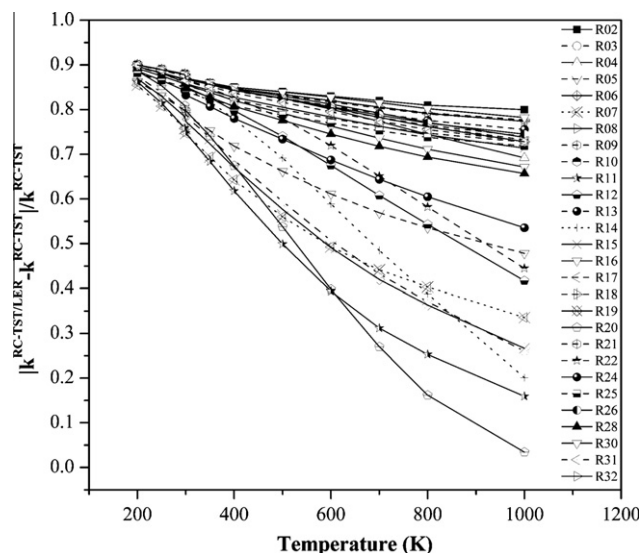
Fig. 8. Relative absolute deviations as functions of the temperature between rate coefficients calculated from explicit full RC-TST and the RC-TST/LER methods.

results in the RC-TST calculation. The fitted equations of hindered rotor correction factors for abstraction of hydrogen from a primary, secondary and tertiary carbon are

$$F_{HR}(T) = 0.2886 + 0.4436 \bigg/ \left[1 + \left(\frac{T}{482.2} \right)^{2.127} \right] \text{ for primary carbon}$$

(11a)

$$F_{HR}(T) = 0.8987 + 0.1093 \bigg/ \left[1 + \left(\frac{T}{591.8} \right)^{4.276} \right] \text{ for secondary carbon}$$

(11b)

$$F_{HR}(T) = 0.8223 + 0.1415 \bigg/ \left[1 + \left(\frac{T}{460.7} \right)^{3.098} \right]$$

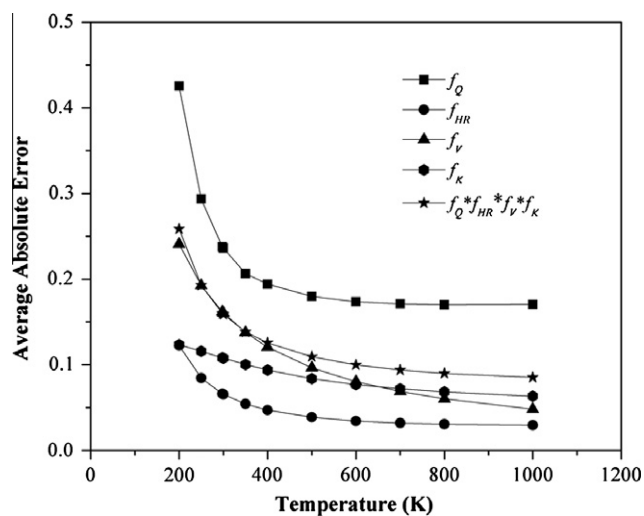for tertiary carbon, respectively.

(11c)

Fig. 9. Averaged absolute errors of the total relative rate factor $f(T)$ (Eq. (2)) and its components namely the tunneling (f_κ), partition (f_Q), potential (f_V) and hindered rotor (f_{HR}) factors as functions of the temperature.
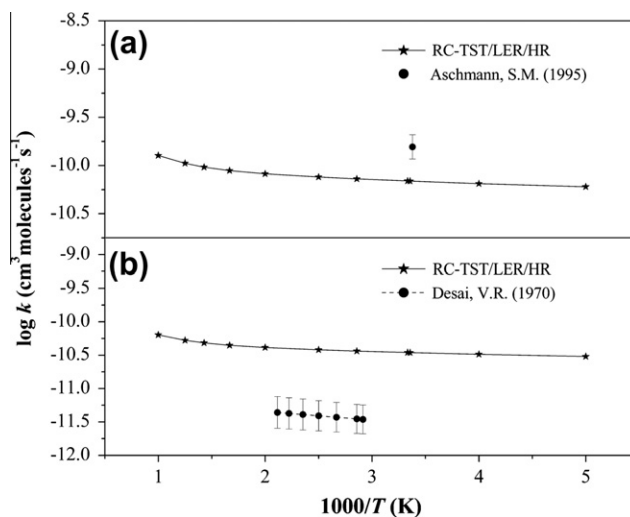

Fig. 10. Arrhenius plots of the predicted rate coefficients using the RC-TST/LER method for $(CH_3)_3CC(CH_3)_3 + Cl \rightarrow HCl + (CH_3)_3CC(CH_3)_2\underline{C}H_2$ reaction (a) and $(CH_3)_3C(CH_2)_3CH_3 + Cl \rightarrow HCl + n\text{-}C_4H_9C(CH_3)_2\underline{C}H_2$ reaction (b) along with an available literature value.

3.4. Prediction of rate coefficients

We now can predict the rate coefficients for all reactions in the representative set in the Cl + alkane class since we have established the necessary parameters – namely, the partition function factor, symmetry number factor, tunneling factor, potential energy factor, and hindered rotor factor using R01 as the reference reaction. The procedure for calculating rate coefficients of any arbitrary reaction in this class is as follow: (i) Calculate f_σ from symmetry numbers of the arbitrary and reference reactions using Eq. (4). (ii) Assign f_Q to be 0.7, 0.4, or 0.3 for abstraction of hydrogen from primary, secondary, or tertiary carbon, respectively. (iii) Calculate $f_\kappa(T)$ from Eqs. (10a), (10b) or (10c) depending to the type of hydrogen abstraction. (iv) The reaction barrier height can be obtained using LER approach by employing Eq. (9a) for AM1 reaction energies or 9b for BH&HLYP reaction energies. $f_V(T)$ is then calculated from Eq. (6) using the barrier height of the reference reaction of 7.526 kcal mol^{-1}. (v) Calculate $f_{HR}(T)$ using Eqs. (11a), (11b) or (11c) according to the type of hydrogen abstraction. (vi) Finally, the rate coefficients of the arbitrary reaction can be calculated by taking the product of the reference reaction rate coefficients given by Eq. (8) with the reaction class factors above. Table 5 summarizes the RC-TST parameters for this reaction class with R01 as the reference reaction. For the sake of comparison, available experiment data by Knox [26], Cadman et al. [27], Beadle and Knox [28], Tschuiho-Raux et al. [29], Qian [30], Pritchard et al. [31], Mitchell and Benson [32] are also compared with our results. A comparison of these data with results predicted in this work is presented in Fig. 7. The agreement between our predicted and those from available experiment data is reasonable. The comparison, however, does not reflect the accuracy of the RC-TST/LER method. Such error analysis is presented below.

3.5. Error analysis

To estimate the overall efficiency of the RC-TST/LER method, we performed two different error analyses. First, we compared the calculated rate coefficients for a selected number of reactions using both the RC-TST/LER and explicit full RC-TST methods. Secondly, we examined the errors in different factors in the RC-TST/LER method. In particular, errors in $f_\kappa(T)$ and $f_{HR}(T)$ are from the

assumption of the same value for the same type of the abstracted hydrogen. Errors in f_Q are from using a constant for all reactions in the class. Errors in $f_V(T)$ are from using the LER expression.

The results from the first analysis are shown in Fig. 8. Here we plotted the relative deviation defined by $(|k^{RC\text{-}TST/LER} - k^{RC\text{-}TST}|/k^{RC\text{-}TST})$ percent versus the temperature for R02–R32 reactions. The relative errors are less than 90% for all reactions. The trend of errors decreases as the temperature increases. It should be noted that this analysis is not precise since the RC-TST/LER is an extrapolation of the μVT/SCT method from Fernández-Ramos et al. [18] as it was used to calculate rate coefficients for the C_2H_5 + Cl reaction not the TST/Eckart/HR. Thus, one can expect larger differences when comparing the RC-TST/LER results to those results calculated directly from explicit full RC-TST method.

The results of the second analysis on the errors from different relative rate factors, namely $f_\kappa(T)$, f_Q, $f_V(T)$ and $f_{HR}(T)$ used in the RC-TST/LER method are shown in Fig. 9. We plotted the absolute errors averaged for R02–R29 reactions. Errors from all components are less than 45% for the temperature range from 200 to 1000 K. The tendency for large errors decreases as the temperature increases. The total errors in the relative rate factors are also less than 25% and decrease as the temperature increases. These are systematic errors of the RC-TST/LER method that can be compared with the results reported by Green et al. [33] using the TST/Wigner to predict the rate coefficients of the reaction using the group additivity (GA) approach. We found that both methods have similar systematic errors. The main difference is that RC-TST/LER method approximates the μVT/SCT level of theory, whereas the GA method approximates only the TST/Wigner level. It is well known that the SCT method is much more accurate on predicting the tunneling coefficient than the simple Wigner method particularly for reactions of the H–L–H (heavy–light–heavy) type.

3.6. Test case

To test our already established RC-TST/LER method, we have selected two reactions which are not in the representative reaction set, namely, (1) $(CH_3)_3CC(CH_3)_3$ + Cl → HCl + $(CH_3)_3CC(CH_3)_2\underline{CH_2}$ reaction and (2) $(CH_3)_3C(CH_2)_3CH_3$ + Cl → HCl + $n\text{-}C_4H_9C(CH_3)_2\underline{CH_2}$ reaction. Both reactions represent hydrogen abstraction from a primary carbon. To calculate the rate coefficients of these two test reactions, only optimizations of reactants and products were carried out at the AM1 level (for reaction energies estimation) with computing time less than one minute. The reaction barrier heights can be calculated employing Eq. (9a) using estimated reaction energies. Other parameters can be also obtained by following the procedure given in Section 3.4 and using formulae in Table 5. Fig. 10 shows the predicted rate coefficients of these two test reactions employing the RC-TST/LER method as shown in Table 5 and the experimental rate coefficient from the available literature of Aschmann and Atkinson [34] and Desai et al. [35]. The agreement between our predicted results and those two suggested experimental data is quite reasonable since the predicted rate coefficients were just estimated from only AM1 reaction energies, reflecting the versatility of RC-TST/LER method.

4. Conclusions

The electronic structures for the 29 hydrogen abstraction reactions in the reaction class of alkane + Cl → HCl + alkyl were performed using quantum mechanics calculation at CCSD(T)/cc-pVDZ//BH and HLYP/cc-pVDZ level. The theoretical rate coefficients in the temperature range 200–1000 K of these reactions in the class were obtained by utilizing transition state theory which included an Eckart tunneling and hindered rotor approximation.

The calculated rate coefficients are in reasonable agreement with available experimental values over the measured temperature range. We have extended our application of the reaction class transition state theory combined with the linear energy relationship (RC-TST/LER) to the prediction of thermal rate coefficients for hydrogen abstraction reactions of alkanes by Cl. The RC-TST/LER has been found to be a promising method for predicting rate coefficients for a large number of reactions in a given reaction class. Our results show that the tunneling correction plays a critical role in the lower temperature range whereas effects of hindered rotors are more important at high temperatures. Our analysis indicates that less than 25% on average absolute error exists in the predicted rate factors using the RC-TST/LER method, while compared to RC-TST explicit rate coefficients the differences are less than 90% on the average. Thus this method would be useful for estimating rate coefficients for reactions involved in complex combustion systems and atmospheric modeling related to the oxidation of alkanes.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.comptc.2013.02.010.

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