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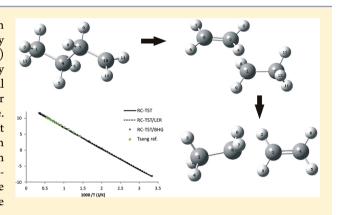
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Kinetics of the C−C Bond Beta Scission Reactions in Alkyl Radical Reaction Class

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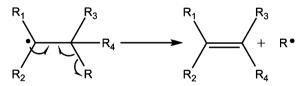[†]Chemistry Institute, University of Bialystok, Hurtowa 1 15-399 Bialystok, Poland

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S *Supporting Information*

ABSTRACT: Kinetics of the β-scission in alkyl radical reaction class was studied using the reaction class transition state theory (RC-TST) combined with the linear energy relationship (LER) and the barrier height grouping (BHG) approach. All necessary parameters were derived from first-principle density functional calculations for a representative set of 21 reactions. Different error analyses and comparisons with available literature data were made. Direct comparison with available experimental data indicates that the RC-TST/LER, where only reaction energy is needed, can predict rate constants for any reaction in this reaction class with excellent accuracy. Specifically for this reaction class, the RC-TST/LER method has less than 60% systematic errors on average in the predicted rate constants when compared to explicit rate calculations.

1. INTRODUCTION

It has long been known that alkyl radical reactions play an important role in the combustion and atmospheric degradation pathways of traditional fuels as well as a wide variety of other chemical processes, including hydrocarbon cracking, pyrolysis, steam cracking, organic synthesis, and partial oxidation.[1−4] Among these reactions, the C−C beta scission as shown below, i.e., breaking of a C−C bond connected between the α carbon radical site and the beta carbon adjacent site, is known to be the most important degradation pathway of the fuel molecules.[5]

Such reactions are also responsible for formation of a number of complex reaction systems. For long-chain alkyl radicals, these direct decomposition reactions are known to compete favorably with the intramolecular isomerization processes. For this reason, for a long time there has been considerable and growing interest in investigating both of these reaction families.[6−32]

In spite of the significant progress made, relatively little information is still known for the kinetics of unimolecular carbonyl radical decomposition reactions. Especially, little is known about the macroscopic features of reactions of long chain and branched alkyl radicals. This is because direct

measurements of the rate constants of decomposition are difficult due to competing multichannel reactions with short-lived and highly reactive intermediates. A series of shock tube results with a quoted uncertainty of less than a factor of 2, for both n-alkyl and branched alkyl radicals, were reported by Tsang and co-workers.[7−9] Due to its importance in combustion of hydrocarbons, Curran reported an extensive review of the literature rate constants coefficients for alkyl and alkoxy radical decomposition, with his own recommendations based on results published previously.[33] There are also a number of theoretical studies on the activation energies, transition state geometries and rate constants of several small alkyl radical decompositions. Jitariu et al.[15,16] studied in detail the C−C beta scissions of n-propyl and 1-pentyl radicals. Threshold energies, bottleneck properties, and the canonical variational transition state theory (CVT) with multidimensional small curvature tunneling (SCT) rates for selected reactions were also reported. Wang et al.[6] theoretically studied competitive unimolecular decomposition and isomerization of 1-hexyl radical. The authors successfully reproduced experimental data reported by Tsang et al.[7] The internal H isomerization channel was found to be dominant over the C−C bond beta scissions in the low temperature regime 250−900 K. A similar conclusion was derived by Curran et al.[1,2] in their series of proposed hydrocarbon combustion mechanisms. However, the alkyl

radical decomposition channel was found to be more important in the high temperature regime ($T > 850$ K). In general, β-scission has been well-accepted as the dominant decomposition path for alkyl radicals. Thus, accurate kinetic data for β-scission of a wide range of alky radicals are of importance.

A common approach used in nearly all kinetic models is to employ systematic rate estimations for well-defined reaction classes. The simplest way is to approximate all reactions in a given class that have the same rate. More accurate methodologies have been also developed in the past. The reaction class transition state theory (RC-TST)[34] extrapolates a known rate constant to that of any arbitrary reaction in the same class using correlations, which are constructed under the TST framework. The key idea of this application is that reactions in the same class have the same reactive moiety whose chemical bonding changes during the course of the reaction, and thus, they are expected to have similarities in their potential energy surfaces along the reaction pathways/valleys. The GA (group additivity) approach is mainly based on the fact that reaction rates depend primarily on the thermodynamic properties of the involved species, for example, the reactants and the corresponding transition state, and that thermal properties can be predicted on the basis of the assumption of group additivity from ab initio calculations in addition to semiexperimental data. This approach was successfully applied by Sumathi et al.,[35−38] Sabbe et al.,[20−23] and Wang et al.[39] Another approach, where rate rules are derived from a systematic investigation of sets of reactions within a given reaction class using electronic structure calculations performed at the CBS-QB3 level of theory, was reported by Villano et al.[40] The survey of the different rate estimation rules was recently reported by Carstensen et al.,[41] and the applicability of the particular approaches is also assessed.

The focus of this study is to provide first-principle based kinetic data for C−C β-scission in a wide range of alkyl radicals using the RC-TST methodology. Recently, Ratkiewicz[26] reported the high pressure limits of the rates constants for the four simple β-scission reactions (i.e., reactions R_1-R_4 from the representative training set given below) using both the RC-TST methodology and the CVT/SCT theory to validate the applicability of RC-TST approach to this class of reaction. The aim of this study is then to obtain all parameters for estimating the rate constants of any C−C bond beta scission of alkyl radicals. This is done by first deriving analytical correlation expressions for rate constants of the reference reaction with those in a small representative set of the class from explicit direct density functional theory (DFT) calculations. The assumption is that these correlation expressions can be extended to all reactions in the class. So far, this assumption has shown to be valid.[24,27,42−46] To develop RC-TST/LER (linear energy relationship) parameters for the title reaction class, the representative set consists of 21 reactions as shown below.

(R_1) p	1-propyl	→	ethene + methyl	
(R_2) p	1-butyl	→	ethene + ethyl	
(R_3) s	2-butyl	→	propene + methyl	
(R_4) p	2-methyl-1-propyl	→	propene + methyl	
(R_5) p	1-pentyl	→	ethene + 1-propyl	
(R_6) s	2-pentyl	→	propene + ethyl	
(R_7) s	3-pentyl	→	1-butene + methyl	
(R_8) p	2-methyl-1-butyl	→	1-butene + methyl	
(R_9) t	2-methyl-2-butyl	→	2-methyl-1-propene + methyl	

(R_{10}) p	2,2-dimethyl-1-propyl	→	2-methyl-1-propene + methyl
(R_{11}) p	2,2-dimethyl-1-butyl	→	2-methyl-1-propene + ethyl
(R_{12}) p	1-hexyl	→	ethene + 1-butyl
(R_{13}) s	2-hexyl	→	propene + 1-propyl
(R_{14}) s	3-hexyl	→	1-pentene + methyl
(R_{15}) p	2-methyl-1-pentyl	→	propene + 1-propyl
(R_{16}) t	2-methyl-2-pentyl	→	2-methyl-1-propene + ethyl
(R_{17}) s	4-methyl-3-pentyl	→	2-pentene + methyl
(R_{18}) t	2,3-dimethyl-2-butyl	→	2-methyl-2-butene + methyl
(R_{19}) s	4-methyl-2-pentyl	→	propene + 2-propyl
(R_{20}) s	3-heptane	→	1-butene + 1-propyl
(R_{21}) p	2,2-dimethyl-1-pentyl	→	2-methyl-1-propene + 1-propyl

The reference reaction is the β-scission of the 1-propyl radical (R_1). Of these 21 reactions, 10 represent C−C bond beta scission of primary (p) C radical (i.e., with radical center located on the primary carbon atom − p type beta scission) and 8 representing beta scissions of secondary (s) and 3 of tertiary (t) carbon alkyls.

2. METHODOLOGY

2.1. Reaction Class Transition State Theory. Since the details of the RC-TST method have been presented elsewhere,[42] we discuss only its main features here. It is based on the realization that the reaction in the same class has 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, by a temperature-dependent function $f(T)$

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

One often would choose the reference reaction to be the smallest reaction in the class, since their rate constants 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

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

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

$$f_\sigma = \frac{\sigma_a}{\sigma_r} \tag{3}$$

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

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

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

$$f_{HR}(T) = \frac{c_{HR,a}(T)}{c_{HR,r}(T)} \qquad (7)$$

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, c_{HR} symbolizes the correction to the total partition function due to the hindered rotation treatment, T is the temperature in Kelvin, and k_B and h are the Boltzmann and Planck constants, respectively. Among these, only the symmetry factor can be easily calculated from the molecular topology of the reactant. Obtaining exact value of four other factors requires structures, energies, and vibrational frequencies of the reactant and transition state for the reaction investigated. The potential-energy factor can be calculated using the reaction barrier heights of the arbitrary reaction and the reference reaction. The RC-TST/LER method uses the linear energy relationship (LER) similar to the well-known Evans Polanyi linear free-energy relationship[47] between classical barrier heights and reaction energies of reactions to estimate reaction barriers and determines the pre-exponential factor (relative to a well-characterized reference reaction) by performing a cost-effective molecular mechanics or DFT calculation with statistical analysis. Furthermore, this variant of the RC-TST method uses averaged values of particular factors (except for symmetry factor) rather than exact values defined by eqs 4–7. As a consequence, RC-TST/LER rates constants are estimated using only reaction energy and reactants topology information; no transition state and frequency calculation are needed. This feature makes the RC-TST/LER method applicable to the different automated mechanisms generation (ARMG) schemes.[48]

2.2. Computational Details. All of the electronic structure calculations were carried out using the Gaussian 09 suite of programs.[49] A hybrid nonlocal density functional theory (DFT), particularly Becke's half and half (BH&H) nonlocal exchange and Lee–Yang–Parr (LYP) nonlocal correlation functionals, has previously been found to be sufficiently accurate for predicting the transition state properties for different classes of reactions.[24–27,42–46] Note 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 for the title reaction family can be accurately predicted by the BH&HLYP method.[26] Geometries of reactants, transition states, and products were thus optimized at the BH&HLYP level of theory with the Dunning's correlation-consistent polarized valence double-ζ basis set [3s2p1d/2s1p] denoted as cc-pVDZ, which is sufficient to capture the physical change along the reaction coordinate for this type of reaction. All reported results for stable molecules as well as transition states were obtained for the lowest energy conformer of a given species. Normal mode analysis was performed at each stationary point to ensure its characteristics; that is, the stable structure has zero imaginary vibrational frequency, whereas the transition state (TS) structure has one imaginary vibrational frequency, whose mode corresponds to the reaction coordinate of the reaction being considered. Geometry, energy, and frequency information were used to derive the RC-TST factors.

To derive the RC-TST correlation functions TST/Eckart rate constants for all reactions in the representative set were calculated. All kinetic calculations were done using the TheRate[50] program. In these calculations overall rotations were treated classically and vibrations treated quantum mechanically within the harmonic approximation except for the modes corresponding to the internal rotations of the CH_3 groups, which were treated as hindered rotations using the method of Ayala et al.[51,52] A previous study by Kungwan et al.[53] on the H abstraction from alkanes reactions class has shown that the contribution of hindered rotations from alkyl groups larger than CH_3 is relatively small due to the cancellation of the treatment within the RC-TST/LER framework (see Figure 1 in ref 42). Thermal rate constants were calculated for the temperature range from 300 to 3000 K, which is sufficient for many combustion applications.

3. RESULTS AND DISCUSSION

In the section below, we first report on the rate constants for the reference reaction and then we describe how the RC-TST factors are derived using the training reaction set. Subsequently, we perform three error analyses to provide some estimates of the accuracy of the RC-TST 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. The second error analysis is a comparison between rate constants calculated by the RC-TST/LER approximation and those from explicit full RC-TST calculations for the whole set. To assess reliability and validity of the correlations, a set of structurally different alkyl radicals, not present in the training set, was also used for this analysis. Final analysis is on the systematic errors from using fitted analytical expressions for the RC-TST/LER correlation functions.

3.1. Rate Constants of the Reference Reaction. The first task for applying the RC-TST method to any reaction class is to have rate constants of the reference reaction as accurate as possible. The rate constants can be from either experimental data or first-principles calculations. In this study the smallest reaction in the title reaction class, called also the principal reaction, namely beta scission of the 1-propyl radical (R_1), is chosen as the reference reaction. Reaction R_1 was extensively studied in ref 26, its rate constants calculated using the canonical variational transition state theory (CVT) with the small curvature tunneling (SCT) method for the temperature range of 300–3000 K were found to agree well with available experimental data. The CVT/SCT derived rate expression for the reference reaction is as follows:[26]

$$k_{CCC\bullet \to C=C+C\bullet} = 8.97 \times 10^{12} T^{0.184} \exp\left(\frac{-15612}{T}\right), \ (s^{-1}) \qquad (8)$$

3.2. Reaction Class Parameters. This section describes how the RC-TST/LER factors were derived using the representative reaction set.

3.2.1. 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 has been shown previously 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.[47] Thus, with 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 the BH&HLYP level of theory. Alternatively, it is possible to approximate all

reactions at the same type of carbon atom site as having the same barrier height, namely the average value. In previous studies[24,44,45] we found that for the different reaction classes, average values of the reaction barriers are dependent on the order of the active carbon site; this approximation was referred to as the barrier height grouping (BHG) approximation. It was suggested in ref 26 that, for the C−C beta scission reaction family, the barrier is dependent on the type (primary, secondary, or tertiary) of the alkyl radical undergoing the reaction. These expectations were confirmed in our DFT calculations, where the titled reaction class can be divided to two subclasses. One consists of only C−C beta scissions of primary (p) and the other includes both the secondary s and tertiary t alkyl radicals. The potential energy factor for each subclass is represented by a different LER. Of the reactions from training set, 10 belong to the p and 11 to the s/t subclasses. The reaction energies and barrier heights for all representative reactions in the representative set are given explicitly in Table 1. The two derived linear energy relation-

Table 1. Classical Reaction Energies, Barrier Heights, and Absolute Deviations between Calculated Barrier Heights from DFT and Semi-Empirical Calculations and Those from LER Expressions and BHG Approach[a]

reaction	ΔE DFT[b]	$\Delta V^{\ddagger}$ DFT[b]	$\Delta V^{\ddagger}$ DFT[c]	$\Delta V^{\ddagger}$ BHG[d]	$|V^{\ddagger} - \Delta V^{\ddagger}_{estimated}|$[e] DFT[c]	$|V^{\ddagger} - \Delta V^{\ddagger}_{estimated}|$[e] BHG[d]
R_1	29.10	35.91	35.52	33.59	0.38	2.31
R_2	26.41	33.89	34.23	33.59	0.34	0.30
R_3	26.61	34.32	34.37	34.64	0.05	0.32
R_4	27.02	35.43	34.57	33.59	0.86	1.84
R_5	26.90	34.22	34.52	33.59	0.29	0.63
R_6	26.60	34.49	34.36	34.64	0.12	0.15
R_7	29.49	36.56	36.84	34.64	0.28	1.91
R_8	25.85	34.63	34.04	33.59	0.59	1.03
R_9	28.43	35.48	35.93	34.64	0.45	0.84
R_{10}	23.03	33.59	32.75	33.59	0.84	0.00
R_{11}	18.19	30.63	30.54	33.59	0.09	2.96
R_{12}	26.72	34.11	34.43	33.59	0.32	0.52
R_{13}	27.09	34.79	34.78	34.64	0.01	0.15
R_{14}	29.45	37.36	36.80	34.64	0.56	2.71
R_{15}	23.12	32.67	32.79	33.59	0.12	0.93
R_{16}	25.54	33.51	33.45	34.64	0.06	1.13
R_{17}	26.45	34.07	34.23	34.64	0.16	0.57
R_{18}	25.94	34.00	33.80	34.64	0.20	0.64
R_{19}	23.46	31.62	31.68	34.64	0.06	3.02
R_{20}	27.18	34.87	34.85	34.64	0.01	0.23
R_{21}	18.50	30.85	30.69	33.59	0.16	2.75
MAD[f]					**0.24**	**1.13**

[a]Zero-point energy correction is not included. Energies are in kcal/mol. [b]Calculated at the BH&HLYP/cc-pVDZ level of theory. [c]Calculated from the LER using reaction energies calculated at the BH&HLYP/cc-pVDZ level of theory: eqs 9a and 9b. [d]Estimated from BHG; $\Delta V^{\ddagger}$ from BH&HLYP/cc-pVDZ calculations. [e]$\Delta V^{\ddagger}_{estimated}$ from the LER using BH&HLYP/cc-pVDZ reaction energies or from BHG. [f]Mean absolute deviations (MAD) for reactions R_2−R_{21}.

ships (one for each subclass) plotted against the reaction energies calculated at the BH&HLYP/cc-pVDZ of theory are shown in Figure 1a,b. These linear fits were obtained using the least-squares fitting method and have the following expressions:
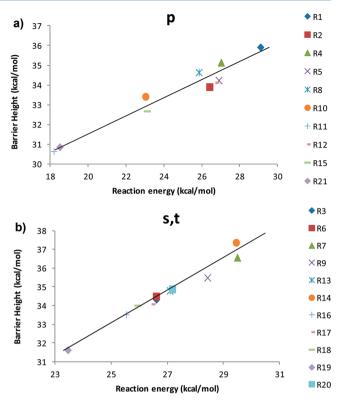

Figure 1. (a and b) Linear energy relationship plot of the barrier heights, $\Delta V^{\ddagger}$ versus the reaction energiesΔE. Both reaction energies and barrier heights and were calculated at the BH&HLYP/cc-pVDZ level of theory.

$$\Delta V_p = 0.4522\Delta E^{BH\&HLYP} + 22.472 \text{ (kcal/mol)}$$

for p alkyl radicals (9a)

$$\Delta V_{s/t} = 0.8551\Delta E^{BH\&HLYP} + 11.616 \text{ (kcal/mol)}$$

for s or t alkyl radicals (9b)

The absolute deviations of reaction barrier heights between the LERs and the direct DFT BH&HLYP/cc-pVDZ calculations are smaller than 0.60 kcal/mol with the medium absolute deviation (MAD) equal to 0.24 kcal/mol (see Table 1). These deviations are, in fact, smaller than the systematic errors of the computed reaction barriers from full electronic structure calculations (see, for example, Table 1 in the ref 26). This is certainly an acceptable level of accuracy for kinetic modeling. Note that in the RC-TST/LER methodology only the relative barrier height is needed. To compute these relative values, the classical barrier height of the reference reaction R_1 calculated at the same level of theory, i.e., BH&HLYP/cc-pVDZ, is needed and has the value of 35.91 kcal/mol.

For the barrier heights grouping (BHG) approach, the average barrier heights are 33.54 and 34.64 kcal/mol with deviations of 1.33 and 1.06 kcal/mol for the p and s/t subclasses, respectively. This deviation is acceptable in the high temperature regime; it may lead to large errors for lower temperatures, however. The key advantage of this approach is that it does not require any additional information to estimate rate constants.

In conclusion, the barrier heights for any reaction in this reaction class can be obtained by using either the LER or BHG approach. The estimated barrier height is then used to calculate

the potential energy factor using eq 6. The performance for such estimations on the whole representative reaction set is discussed in the error analyses below.

3.2.2. Reaction Symmetry Number Factor. The reaction symmetry number factors f_σ were calculated simply from the ratio of reaction symmetry numbers of the arbitrary and reference reactions using eq 3. The reaction symmetry number of a reaction is given by the number of symmetrically equivalent reaction paths. For the C−C bond beta scission reaction class this number is mainly equal to 1. Only for symmetric alkyl radicals with odd number of carbons in the main chain and radical center located in the middle of the main chain, this value may differ from unity. Of the 21 reactions in the training set, 20 processes possess symmetry factor equal to 1; only for R_7 f_σ is equal to 2.

3.2.3. Tunneling Factor. The tunneling factor f_κ is the ratio of the transmission coefficient of reaction R_a to that of the reference reaction R_r. Due to cancellation of errors in calculations of the tunneling factors, we have shown that the factor f_κ can be reasonably estimated using the one-dimension Eckart method.[42] We found that the tunneling factors are close to unity for both subclasses and are nearly temperature independent. The largest deviation from unity is about 5%. This is due to the fact that tunneling is not very significant for β-scission reactions. For this reason, we can assume the tunneling factor is unity for this reaction

3.2.4. Partition Function Factor. The partition factor is the product of the translational, rotational, internal rotation, vibrational, and electronic component. The translational and rotational factors are temperature-independent. As pointed out in our previous study,[42,44] the temperature-dependent part of the total partition function factor f_Q mainly originates from the differences in the coupling between the substituents with the reactive moiety and its temperature dependence, which arises from the vibrational component and internal rotations only. Note that since contributions from the hindered rotation modes are treated separately, they are not included in these partition function factors. The temperature dependent partition factor is averaged over all reactions of a given subclass. Averaged partition function factors for the two subclasses, calculated over the temperature range of 300−3000 K, are shown in Figure 2 and were fitted to analytical expressions as given below:

$$f_Q^p = 1.14 - 0.69 \exp(-T/285.19) \text{ for p alkyl radicals}$$

$$(10a)$$

$$f_Q^{s,t} = 1.25 - 1.08 \exp(-T/273.28) \text{ for s or t alkyl radicals}$$

$$(10b)$$

Figure 2 shows the average value of partition function factors for the two subclasses differs substantially. As mentioned earlier, the coupling between substituents with the reactive moiety is believed to account for these differences.

3.2.5. Hindered Rotation Factor. It is important to point out that the motion of the internal rotation of the methyl group in the reactive moiety, internal rotors gain and loss in the course of the reaction, and contributions from different transition state rotational conformers are already treated explicitly in the rate constants of the reference 1-propyl → ethene + methyl reaction.[26] Thus, the reaction class factor due to these hindered rotations is a measure of the substituent effects on the rate constant from the hindered rotors relative to that of the reference reaction R_1. We used the approach
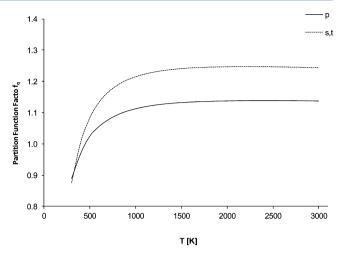

Figure 2. Plots of the averaged values of the partition function factor for p and s/t type β-scissions.

proposed by Ayala and Schlegel[51] to calculate the hindered rotation correction factor to the partition function for a certain vibrational mode. In this case, the rotating group, the periodicity number of the torsional potential of the vibrational mode, geometry of the molecule is needed. Previous study by Kungwan and Truong[53] shown that the relative contribution of hindered rotations from alkyl groups larger than CH_3 is small due to the cancellation of the treatment within the RC-TST framework. For this reason, in this study we consider hindered rotation treatment for the $-CH_3$ and $-C_2H_5$ groups. The latter is to validate the previous finding for this reaction class. For C−C beta-scission reaction, the rotatable C−C bond neighboring to the active C−C bond transforms from an sp^3 configuration in the reactants to an sp^2 one in the products and thus its effects at the transition state may complicate the use of a simple empirical relationship. We found, that the rotational potential barriers depend slightly on the type of the carbon atom to which the methyl group is directly connected. These barriers were found to be 3.3, 3.5, and 3.9 kcal/mol for the $-CH_3$ groups bonded to secondary, tertiary, and quaternary sp^3 C atoms, respectively, and 3.8 kcal/mol for the methyl group bonded to sp^2 C atom. Within any of these four sets, differences in the barriers were found to be negligible, i.e. less than 0.3 kcal/mol. Rotational barriers for the low frequency rotation of the $-C_2H_5$ group is slightly more complicated, however. The highest barrier does not exceed 6 kcal/mol. The potential energy curves for both of these kinds of internal rotations are plotted on the Figures S1 and S2 in the Supporting Information. The effect of the hindered rotation treatment to total rate constants can be seen in Figure 3. The ethyl group rotations were found to exert a noticeable influence only on the branched alkyl radicals, for which gauche interactions are important. Individual factors for particular reactions R_2−R_{21}, tantamount to the k_{HO}/k_{HR} values for these reactions, are listed in the Table S1 of the Supporting Information. It can be seen from Figure 3 that both HR correction factors are slightly temperature dependent though the magnitude of these correction factors are larger than 0.8 for temperatures above the room temperature. For the linear radicals the average value is closer to 1 with a flat minimum in the 1000−1100 K region. For the branched species HR factor is generally smaller than those for n-alkyls by about 10%. Thus, neglecting internal rotations of larger alkyl groups may lead to an error on the
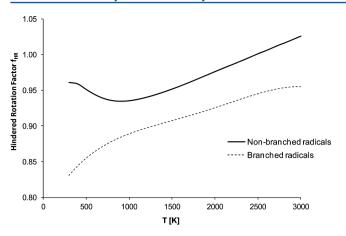
Figure 3. Average hindered rotation corrections to the total rate constants for all reactions in the temperature range of 300−3000 K.

order 10% in the rate constant. The average values of these HR factors are fitted to analytical expressions as given below:

$$f_{\mathrm{HR,n-alkyls}} = 2 \times 10^{-8}T^2 - 3.3 \times 10^{-5}T + 0.96$$

$$\text{for n-alkyl radicals} \qquad (11a)$$

$$f_{\mathrm{HR,branched\ alkyls}} = 0.528T^{0.0613} \text{ for branched alkyl radicals}$$

$$(11b)$$

Since subclasses defined with regard to calculation of the HR factor does not match these defined for other factors, applications of these results in any automated reaction generation procedure would be difficult. Our suggestion is to

neglect the low frequency motions of groups larger than −CH₃, formula 11a should be then applied to the whole reaction class.

3.3. Prediction of Rate Constants. What we have established so far are the necessary parameters, namely potential energy factor, reaction symmetry number factor, tunneling factor, and partition function factor, for application of the RC-TST/LER theory to predict rate constants for any reaction in the C−C beta scission in alkyl radicals reaction class. The procedure for calculating rate constants of an arbitrary reaction in this class is (i) calculate the potential energy factor using eq 6 with the $\Delta V_r^{\ddagger}$ value of 35.91 kcal/mol. The reaction barrier height can be obtained using the LER approach by employing eqs 9a and 9b for BH&HLYP/cc-pVDZ reaction energies or by the BHG approach; (ii) determine the symmetry number factor from eq 3; (iii) evaluate the partition function factor using eqs 10a and 10b; (iv) evaluate hindered rotation factor using eqs 11a and 11b; and (v) the rate constants of the arbitrary reaction can be calculated by taking the product of the reference reaction rate constant given by eq 8 with the reaction class factors above. Table 2 summarizes the RC-TST/LER parameters for this reaction class. If the BHG barrier heights and average values for other factors are used, the rate constants are denoted by RC-TST/BHG. The RC-TST/BHG rate constants for any reactions belonging to this class can be estimated without any further calculations as

$$k(T) = \sigma_a \times 1.60 \times 10^{13}T^{0.13} \exp\left(\frac{-14534}{T}\right)(s^{-1})$$

$$\text{for p alkyl radicals} \qquad (12a)$$

Table 2. Parameters and Formulations of the RC-TST/LER Method for C−C Bond Beta Scission in Alkyl Radicals Reaction Class[a]

$$k_a(T) = k_p(T) \cdot f_\kappa(T) \cdot f_Q(T) \cdot f_{HR}(T) \cdot f_\nu(T) \cdot f_\sigma ; f_\nu(T)$$

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

T is in Kelvin; $\Delta V^{\ddagger}$ and ΔE are in kcal/mol; zero-point energy correction is not included

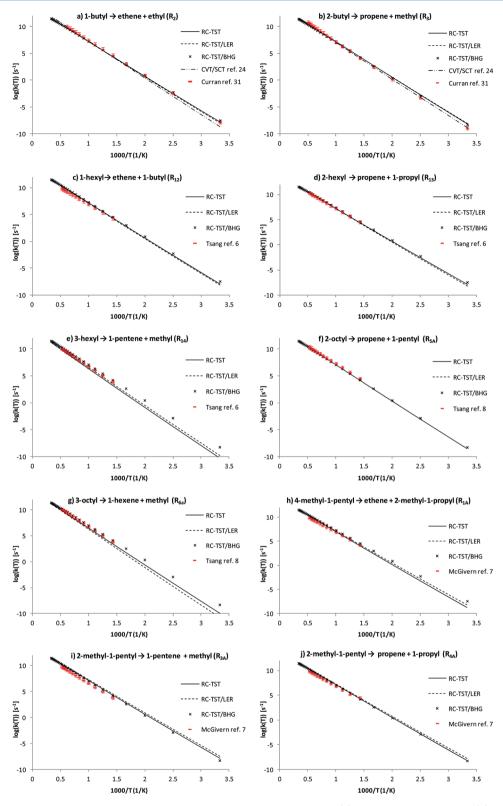|	
f_σ	calculated explicitly from the symmetry of reactions (see eq 3)
$f_\kappa(T)$	$f_\kappa = 1$
$f_Q(T)$	$f_Q^p = 1.14 - 0.69 \exp(-T/285.19)$ for p type β-scissions
	$f_Q^{s,t} = 1.25 - 1.08 \exp(-T/273.28)$ for s/t type β-scissions
$f_{HR}(T)$	$f_{\mathrm{HR,n-alkyls}} = 2 \times 10^{-8}T^2 - 3.3 \times 10^{-5}T + 0.96$ for n-alkyl radicals
	$f_{\mathrm{HR,branched\ alkyls}} = 0.528T^{0.0613}$ for branched alkyl radicals
$\Delta V^{\ddagger}$	LER $\qquad V_p = 0.4522 \times \Delta E^{\mathrm{BH\&HLYP}} + 22.472$ (kcal/mol) for p type β-scissions
	$\Delta V_{s,t} = 0.8551 \times \Delta E^{\mathrm{BH\&HLYP}} + 11.616$ (kcal/mol) for s/t type β-scissions
	$\Delta V_r^{\ddagger} = 35.91$ kcal/mol
$k_p(T)$	$k_{\mathrm{CCC\bullet \rightarrow C=C+C\bullet}} = 8.97 \times 10^{12}T^{0.184} \exp\left(\frac{-15612}{T}\right)(s^{-1})$
	BHG approach $\qquad k(T) = \sigma_a \times 1.60 \times 10^{13}T^{0.13} \exp\left(\frac{-14534}{T}\right)(s^{-1})$ for p type β-scissions
	$k(T) = \sigma_a \times 1.38 \times 10^{13}T^{0.17} \exp\left(\frac{-15054}{T}\right)(s^{-1})$ for s/t type β-scissions

[a]1-Propyl→ ethene + methyl is the reference reaction.

Figure 4. Arrhenius plots of the calculated and experimental rate constants for the reactions: (a) 1-butyl → ethene + ethyl, (b) 2-butyl → propene + methyl, (c) 1-hexyl → ethene + 1-butyl, (d) 2-hexyl → propene + 1-propyl, (e) 3-hexyl → 1-pentene + methyl, (f) 2-octyl → propene + 1-pentyl, (g) 3-octyl → 1-heptene + methyl, (h) 4-methyl-1-pentyl → ethene + 2-methyl-1-propyl, (i) 2-methyl-1-pentyl → 1-pentene + methyl, (j) 2-methyl-1-pentyl → propene + 1-propyl. Experimental data are taken from: ref 33 for reactions a and b, ref 7 for reactions c−e, ref 9 for reactions f and g, and ref 8 for reactions h−j.
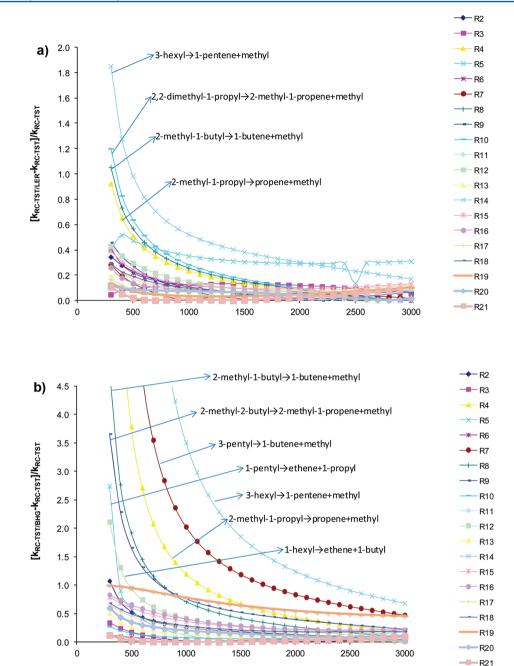
Figure 5. (a and b) Relative absolute deviations as functions of the temperature between rate constants calculated from explicit TST/Eckart calculations for all selected reactions and (a) from the RC-TST/LER method where BH&HLYP reaction energies were used for the LER and (b) from the RCT-TST/BHG method.

$$k(T) = \sigma_a \times 1.38 \times 10^{13} T^{0.17} \exp\left(\frac{-15054}{T}\right) \ (s^{-1})$$

for s or t alkyl radicals (12b)

The appropriate symmetry factor of 1 are included in the rate constant expressions above. The use of these equations for a target reaction requires multiplication with its proper symmetry number σ_a. For 20 among 21 reactions from the representative set $\sigma_a = 1$ only one (namely R$_7$) has $\sigma_a = 2$.

3.4. Error Analyses. As mentioned earlier, only a limited amount of the experimental data is available for C–C beta scissions in alkyl radicals. In ref 26, CVT/SCT calculations for four simplest reactions within the title family were reported,

results were compared with Curran recommendation.[33] In this study, two of these rates, namely reactions R$_2$ and R$_3$ from the training set, are also calculated with RCT-TST/LER method. Moreover, experimental data are available for the reactions R$_{12}$, R$_{13}$, and R$_{14}$ from the training set and five other C–C bond β-scission reactions, not present in the training set

2-octyl → propene + 1-pentyl (R22)

3-octyl → heptene + methyl (R23)

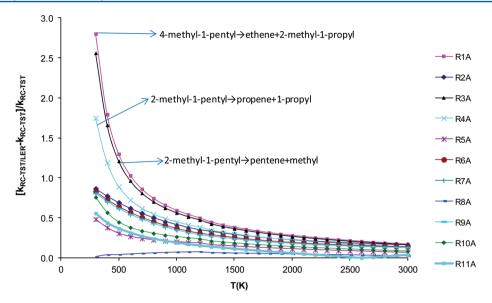4-methyl-1-pentyl → ethene + 2-methyl − 1-propyl (R24)

Figure 6. Relative absolute deviations as functions of the temperature between rate constants calculated from explicit full RC-TST calculations for the reactions R_{1A}–R_{11A} and from the RC-TST/LER method where BH&HLYP reaction energies were used for the LER.

2-methyl-1-pentyl → 1-pentene + methyl   (R25)

2-methyl-1-pentyl → propene + 1-propyl   (R26)

among other C−C bond beta scissions in hexyl, octyl, and 4-methyl-1-pentyl radicals done by Tsang et al.[7,9] and McGivern et al.[8] The experiments were performed in single pulse shock tube at temperatures in the 850−1000 K range. High-pressure rate constants have been derived over 700−1900 K range with an uncertainty factor of less than 2. The value of a given rate constant, k, could lie between k_m/f and $k_m f$, where k_m is the reported value and f is an uncertainty factor. A comparison of these data with results reported in this study is presented in the Figure 4a−j. In this Figure, RC-TST labeled curves represent results obtained within the full RC-TST methodology, using eqs 3−7 to extrapolate high pressure limits of rate constants calculated for the reference reaction R_1 to those presented in the Figure 4. To obtain these results, the knowledge of the transition state is necessary, whereas only reaction energy is needed in the RC-TST/LER approximation. For small alkyls (reactions R_2 and R_3), the agreement of the RC-TST results with both high level CVT/SCT calculations[26] and latest Curran recommendations[33] is quite satisfactory, there is an observable difference in the high temperature regime, however. As can be further seen from the Figure 4, the agreement between the RC-TST and RC-TST/LER results and the experimentally derived data (refs 7−9) is, for the reactions $R_{2−3}$ (reaction R_2 through reaction R_3), $R_{12−14}$, R_{1A}, R_{3A}, and R_{4A-6A}, quite excellent. The experimental data were actually derived for temperatures from 850 to 1000K, then extrapolated to the 700−1900K regime. Among 10 reactions considered, RC-TST curves for 8 reactions (except for R_{14}, Figure 4e, and R_{3A}, Figure 4i) lie within experimental error bars in the 850−1000K regime. Similarly, only two RC-TST/LER curves (namely R_{6A}, Figure 4g, and R_{3A}, Figure 4i) do not lie within the experimental error bars in the temperature regime the experimental data were actually obtained. The agreement is noticeable worse for the RC-TST/BHG approach, assuming one averaged barrier height per specific reaction site, however. This approach introduces a noticeable error for some reactions (Figure 4e,g,h), especially in the low temperature regime, thus its use is not recommended.

The systematic errors introduced by the LER and BHG approaches are discussed in detail in the next error analysis, which compares RC-TST/LER and RC-TST/BHG results with those from explicit calculations. As mentioned in our previous studies,[34,42] the RC-TST methodology can be thought of as a procedure for extrapolating rate constants of the reference reaction to those of any reaction in the class. Comparisons between the calculated rate constants for a small number of reactions using both the RC-TST/LER or RC-TST/BHG and the full RC-TST methods provide additional information on the accuracy of the LER and BHG approximations. The results for this error analysis for 21 representative reactions, (i.e., the comparisons between the RC-TST/LER and full RC-TST methods) are shown in Figure 5a, wherein the relative deviation defined by $(|k^{RC\text{-}TST} - k^{RC\text{-}TST/LER}|/k^{RC\text{-}TST})$ as a percent versus the temperature for all reactions in the representative set, R_2–R_{21} is plotted. Curves for reactions showing errors larger than 100% were explicitly labeled by its reactions on the plot. For the temperatures >1000 K all the reactions in this set, the unsigned relative errors are within 45%. In the low temperatures regime, four reactions have errors larger than 100%. So, in general, it can be concluded that RC-TST/LER can estimate thermal rate constants for reactions in this class within 50% when compared to those calculated explicitly using the full RC-TST method. For other cases, explicitly marked in Figure 5, maximum error is less than 200% which may be still an acceptable if such reactions are not sensitive for a given reacting condition. Similar analysis is presented for the RC-TST/BHG approach as shown in Figure 5b. As expected, RC-TST/BHG has the larger errors in the low temperature regime, specifically 7 from 21 reactions have the maximum error significantly exceeds 100%. Among these 7 reactions, 5 exhibit very large error, which may significantly affect the accuracy of the RC-TST/BHG method, especially in the low temperature regime. Note that the convenience of ready to be used rate expressions for any reaction in the class, may still offset the less accuracy of the BHG approach compared to that of the LER.

To demonstrate the reliability of the correlations, further validation is needed to verify that the 21 reaction representative set selected for developing the RC-TST/LER parameters is
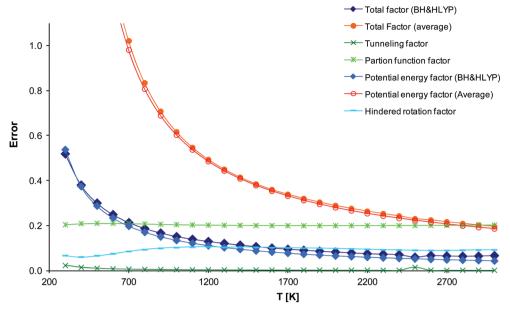
Figure 7. Averaged absolute errors of the total relative rate factors $f(T)$ (eq 2) and its components, namely the partition function (f_Q), potential energy (f_V), and hindered rotation (f_{HR}) factors as functions of temperature.

sufficient to represent this reaction class. We calculated the relative deviation defined by ($|k^{RC-TST} - k^{RC-TST/LER}|/k^{RC-TST}$) for 11 additional reactions, not included in the training set. The results are plotted in Figure 6. In particular, these reactions are shown below.

(R$_{1A}$)	4-methyl-1-pentyl	→	ethene + 2-methyl-1-propyl
(R$_{2A}$)	2-methyl-2-pentyl	→	2-methyl-1-propene + ethyl
(R$_{3A}$)	2-methyl-1-pentyl	→	pentene + methyl
(R$_{4A}$)	2-methyl-1-pentyl	→	propene + 1-propyl
(R$_{5A}$)	2-octyl	→	propene + 1-pentyl
(R$_{6A}$)	3-octyl	→	1-heptene + methyl
(R$_{7A}$)	2,2,4-trimethyl-1-pentyl	→	2-methyl-1-propene + 2-methyl-1-propyl
(R$_{8A}$)	2,2,4-trimethyl-1-pentyl	→	2,4-dimethyl-1-pentene + methyl
(R$_{9A}$)	2,4,4-trimethyl-1-pentyl	→	propene + 2,2-dimethyl-1-propyl
(R$_{10A}$)	2,2,4-trimethyl-1-pentyl	→	4,4-dimethyl-1-pentene + methyl
(R$_{11A}$)	2,2-diethyl-1-butyl	→	2-ethyl-1-butene + ethyl

Of the reactions R$_{1A}$-R$_{11A}$, those with 2,2,4-trimethyl-1-pentyl (isooctyl) radicals (reactions R$_{7A}$ − R$_{11A}$), which are currently used to model branched alkanes in diesel fuel surrogates,[2] are of particular interest to the combustion community. As can be seen from Figure 6, kinetic data for these β-scissions from highly branched alkyls can be accurately estimated by the RC-TST/LER method. Note that the error for the reaction R$_{4A}$ is noticeably larger than others. However, it is within the same range as for reactions from the training set (R$_2$−R$_{21}$), thus proving the validity of the RC-TST/LER approximation.

Finally, an analysis on the systematic errors in different factors in the RC-TST/LER methods was performed. The total error is affected by the errors in the approximations in the potential energy factor, partition function factor and hindered rotation factor introduced in the method. The deviations/errors between the approximated and exact factors within the TST framework are calculated at each temperature for every reaction in the representative set and then averaged over the whole class.

For the LER approach error in the potential energy factor comes from the use of an LER expression; that of the partition function factor, from using eqs 10a and 10b, and that of the hindered rotation factor from using eq 11. Absolute errors averaged over all 20 reactions, R$_2$−R$_{21}$ as functions of the temperature are plotted in Figure 7. In this figure, BH&HLYP means errors resulting from using individual BH&HLYP reaction barriers and average mean using an average barrier for all reactions within the subclass. The error introduced by the partition function factor is the largest of individual factors for T > 500 K, roughly around 20% for the whole temperature range. For T > 800 K this factor gives error bigger than a total factor, which can be explained by mutual error cancelation.

Inspection of the Table 1 and Figure 5a,b suggest, that error of the potential energy factor introduced by the BHG approximation is significantly larger than that resulting from the LER approach. Indeed, for T < 700 K error of the BHG potential energy factor is noticeable and exceeds 100%. This also affects the low-temperature behavior of the total BHG factor, which exceeds 500% for T < 500 K. In contrast, both LER factors (i.e., potential energy and total) exhibit errors less than 60% even at the low temperature regime, these errors decrease as the temperature increases to reach almost constant value of ∼10% for T < 1200 K. As can be concluded from Figure 5b, the huge error of the BHG factors mainly comes from only 4 reactions. This observation confirms the previous conclusions that the BHG approach may be risky for T < 1000 K, and the LER approximation should be used at the low temperatures instead. This approach shows noticeable lower error in the potential energy and total factors than the BHG approximation in the whole temperature range. For temperature range T > 1000 K all of the errors, except for these of the BHG method, are almost constant. Further, except for the BHG approach, the total systematic errors due to the use of simple analytical expressions for different reaction class factors are less than 60% for the temperature range 300−3000 K. Performance for the RC-TST/BHG method is significantly worse; this method is rather not recommended for using for T < 1000 K. The failure of the BHG method for the title reaction

class is due by the inadequacy of basic assumption underlying this approximation, namely simple dependence of the barrier height on the type of reaction site. As the reaction barrier depends not only on the kind of C−C bond broken in the course of reaction, but also on the other issues, like presence of carbonyl substituents in the case of branched alkyl radicals or conformation. For these reasons the BHG approach is, in general, not recommended for the title reaction class, especially for branched alkyls. As may be observed in Figure 4h−j, the RC-TST/LER approach works quite well even for branched radicals, however.

3.5. Summary of Approximations Used in the RC-TST Method. By generalizing from the small reference reaction to larger homologues and, consequently, enabling the obtaining of any rates constants within a given reaction class with accuracy comparable to high level methods but at the fraction of the cost, the RS-TST method provides an effective way to derive considerable benefits from expensive electronic structure calculations. However, the user should be aware of approximations used. In particular, these are as follows:

- Accuracy of RC-TST rate constants depends on the accuracy of the rate constants of the reference reaction. Thus, each improvement in the rate measurement/ calculation methodology results in considerable enhancement of the predicted rates.

- The recrossing effect is taken into account only in part, corresponding to those in the reference reaction. The "additional" recrossing trajectories, not included in the reference reaction rate constants, are neglected. As shown in ref 26, the variational effects are not important for the title reaction class, thus this approximation does not affect the RC-TST results.

- Although absolute transmission coefficients for hydrogen abstraction reactions often require multidimensional tunneling methods to account for the large corner-cutting effects, it was shown[42] that, because of cancellation of errors, the tunneling factor f_κ can be accurately predicted using the 1-D Eckart method, as it is done in the RC-TST approach. For this reaction class, tunneling corrections calculated for the reference reaction can be used for all reactions in the class.

- The RC-TST method does not fully take into account conformational aspects. For this reaction class, it assumed the effects of hindered rotation of different side chains are the same as of the methyl group. Such simplification may yield noticeable error in some of the reactions within the family. It is illustrated by the differences in hindered rotation factors for the methyl and ethyl groups attached at different carbon types.

- Since the number of hindered rotation modes may be different for reactants and products, the f_{HR} factor, based on the averaged value of eq 11, may not be relevant for some reactions. However, as shown in Figure 3, this error is not significant for the title reaction class; errors from using harmonic approximations are mostly canceled.

- The barrier height for any reaction within the family is calculated with the LER. Although, as shown in Table 1, error associated with this approximation is not large, it may affect the low-temperature value of the potential energy factor f_v and, consequently, the RC-TST/LER rate constants.

4. CONCLUSION

The application of the reaction class transition state theory combined with the linear energy relationship and the barrier height grouping approach to the prediction of thermal rate constants for C−C bond beta scission reaction class was carried out. The rate constants for the reference reaction 1-propyl → ethene + methyl were obtained by the CVT/SCT method in the temperature range 300−3000 K. The RC-TST/LER, where only reaction energy is needed, was found to be promising method for predicting rate constants for any reaction in this reaction class. The error analyses indicate that the RC-TST/ LER method can predict rate constants within a factor of 2 compared to explicit rate calculations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete author list of ref 49, the explicit values of the hindered rotations (HR) factor for reactions R_2−R_{21}, and rotational energy profiles used for determining these factors. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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