Kinetics of Hydrogen Abstraction Reaction Class H + H−C(sp^3): First-Principles Predictions Using the Reaction Class Transition State Theory

Shaowen Zhang and Thanh N. Truong*

Henry Eyring Center for Theoretical Chemistry, Department of Chemistry, University of Utah, 315 S. 1400 E., Room 2020, Salt Lake City, Utah 84112

Received: May 21, 2002; In Final Form: November 25, 2002

We present an application of the reaction class transition state theory (RC-TST) in predicting thermal rate constants of the hydrogen abstraction reactions H + H−C(sp^3) where C(sp^3) is a saturated carbon atom. Combining the RC-TST with the linear energy relationship (LER) allows rate constants of any reaction in the class to be estimated from only reaction energy information. We have derived from first-principles all parameters for the RC-TST/LER method so rate constants for any reaction in this class can be predicted from only reaction energy, that can easily be computed from either the density functional theory or semiempirical molecular orbital theory. We have performed error analyses for a large number of reactions in the above class for which some experimental measurements or estimates are available. By comparisons with results from full TST/Eckart calculations we also found the RC-TST/LER method is quite cost-effective and has accuracy comparable to first-principles predictions using more rigorous methodologies.

I. Introduction

Hydrogen abstractions of hydrocarbons by hydrogen atoms, $H + RH \rightarrow H_2 + R$, belong to an important class of reactions in combustion chemistry. Particularly, under pyrolytic conditions (in the absence of oxidants), hydrogen atoms can be the primary chain carriers in thermal decomposition of hydrocarbons. Despite its significance, there are only about 10 of such elementary reactions where some experimental kinetic data are available. Yet there are only one to two of these reactions where such data are known with some level of accuracy.[1−7] For reactions involving alkanes and alkenes larger than C2, there are multiple pathways. At the present time, there is no data on the branching ratios. A major difficulty in the experimental study of such reactions is the possibility of secondary step reactions involving the intermediate alkyl radicals R to occur faster than the first step. In such a case, theory can play an important role in providing necessary kinetic information. However, to the best of our knowledge at the present time, theoretical kinetic information is available only for a small number of such reactions, particularly for reactions with methane,[3,8−12] propene,[13] *n*-butane,[14] and benzene.[15,16] To obtain rate constants for larger alkanes, Baldwin and Walker[17] proposed a general expression for the H + RH reactions as a sum of hydrogen abstraction from primary, secondary and tertiary carbons.

Cohen[18] later used a thermo-chemical kinetics formulation of the conventional transition state theory (TST) to analyze available experimental rate constants and to propose an approximate scheme for extrapolating thermal rate constants to a wider temperature range for a small number of reactions in the H + RH reaction class. The author arrived at a very different general expression for the rate constants of the H + RH reactions even both of these expressions assume that, for each type of hydrogen abstraction, the rate constants are the same for all alkanes. The assumption that the overall rate constants can be obtained by adding rate constants of all possible primary, secondary, and tertiary hydrogen abstraction reactions has not been proven and tested theoretically. It is interesting to note that such an assumption was later found invalid for the OH + RH reaction class by Cohen in a separate report.[19] Hence, the thermal rate constants are not additive in general or, at least, not in the approach used by Cohen.

Recently, we introduced a new theory called reaction class transition state theory (RC-TST) for predictions of thermal rate constants for a large number of reactions in a given class.[20] The RC-TST method recognizes that reactions in a given class have the same reactive moiety; therefore, their potential energy surfaces along the reaction coordinate are very similar and thus can be extrapolated from one to the others. The RC-TST theory provides a rigorous methodology for estimating thermal rate constants of any reaction from the smallest reaction (i.e., the principal reaction) in the class and from the differences in the classical barriers and reaction energies. As shown in our previous studies,[21,22] such energy differences can be obtained from a relatively low level of electronic structure theory.

The reaction class concept was recently employed by Green and co-workers[23,24] for developing group additivity contributions of transition states in estimating thermal rate constants of reactions in a given class. The approach was shown to be rather promising. The differences between Green's group additivity approach and the RC-TST method employed in this study are discussed in the results and discussion section below.

In this study, we extended the RC-TST theory one step further by showing that within the reaction class framework there is a linear-energy-relationship (LER) between the classical barrier and the reaction energy. Consequently, it is possible to predict rate constants of any reaction in the class by knowing only the reaction energy of such a reaction. We illustrate the RC-TST/LER theory by attempting to predict rate constants for a large number of hydrogen abstraction reactions belonging to a given class and then compare them to available experimental data or estimates. In particular, 46 hydrogen abstraction reactions

* To whom correspondence should be addressed.

10.1021/jp021265y CCC: $25.00
Published on Web 01/30/2003

involving 23 different hydrocarbons were studied. All of these reactions belong to the same reaction class given below:

$$H + H{-}C(sp^3) \rightarrow H_2 + {}^{\bullet}C(sp^3)$$

C(sp^3) denotes carbon atom with sp^3 bonding. However, they can be separated into two sub-groups: one is the reaction of H with alkanes (R1 ∼ R14) and the other is the reaction of H with alkenes that form resonant stabilized transition states and radicals (R15 ∼ R23)

$$H + CH_4 \rightarrow H_2 + CH_3 \quad \text{(R1)}$$

$$H + C_2H_6 \rightarrow H_2 + C_2H_5 \quad \text{(R2)}$$

$$H + C_3H_8 \rightarrow H_2 + n\text{-}C_3H_7 \quad \text{(R3a)}$$

$$\rightarrow H_2 + s\text{-}C_3H_7 \quad \text{(R3b)}$$

$$H + C_4H_{10} \rightarrow H_2 + n\text{-}C_4H_9 \quad \text{(R4a)}$$

$$\rightarrow H_2 + s\text{-}C_4H_9 \quad \text{(R4b)}$$

$$H + (CH_3)_3CH \rightarrow H_2 + (CH_3)_2CHCH_2 \quad \text{(R5a)}$$

$$\rightarrow H_2 + (CH_3)_3C \quad \text{(R5b)}$$

$$H + n\text{-}C_5H_{12} \rightarrow H_2 + 1\text{-}C_5H_{11} \quad \text{(R6a)}$$

$$\rightarrow H_2 + 2\text{-}C_5H_{11} \quad \text{(R6b)}$$

$$\rightarrow H_2 + 3\text{-}C_5H_{11} \quad \text{(R6c)}$$

$$H + (CH_3)_4C \rightarrow H_2 + (CH_3)_3CCH_2 \quad \text{(R7)}$$

$$H + (CH_3)_2CHCH_2CH_3 \rightarrow H_2 + (CH_3)_2CHCH_2CH_2 \quad \text{(R8a)}$$

$$\rightarrow H_2 + CH_3CH(CH_2)CH_2CH_3 \quad \text{(R8b)}$$

$$\rightarrow H_2 + (CH_3)_2CHCHCH_3 \quad \text{(R8c)}$$

$$\rightarrow H_2 + (CH_3)_2CCH_2CH_2 \quad \text{(R8d)}$$

$$H + n\text{-}C_6H_{14} \rightarrow H_2 + 1\text{-}C_6H_{13} \quad \text{(R9a)}$$

$$\rightarrow H_2 + 2\text{-}C_6H_{13} \quad \text{(R9b)}$$

$$\rightarrow H_2 + 3\text{-}C_6H_{13} \quad \text{(R9c)}$$

$$H + CH_3CH_2C(CH_3)_3 \rightarrow H_2 + CH_2CH_2C(CH_3)_3 \quad \text{(R10a)}$$

$$\rightarrow H_2 + CH_3CH_2C(CH_3)_2CH_2 \quad \text{(R10b)}$$

$$\rightarrow H_2 + CH_3CHC(CH_3)_3 \quad \text{(R10c)}$$

$$H + (CH_3)_2CHCH(CH_3)_2 \rightarrow H_2 + CH_2CH(CH_3)CH(CH_3)_2 \quad \text{(R11a)}$$

$$\rightarrow H_2 + (CH_3)_2CCH(CH_3)_2 \quad \text{(R11b)}$$

$$H + (CH_3)_2CHCH_2CH_2CH_3 \rightarrow H_2 + (CH_3)_2CHCH_2CH_2CH_2 \quad \text{(R12a)}$$

$$\rightarrow H_2 + (CH_3)_2CHCH_2CHCH_3 \quad \text{(R12b)}$$

$$\rightarrow H_2 + (CH_3)_2CHCHCH_2CH_3 \quad \text{(R12c)}$$

$$\rightarrow H_2 + (CH_3)_2CCH_2CH_2CH_3 \quad \text{(R12d)}$$

$$\rightarrow H_2 + CH_3CH(CH_2)CH_2CH_2CH_3 \quad \text{(R12e)}$$

$$H + n\text{-}C_7H_{16} \rightarrow H_2 + 1\text{-}C_7H_{15} \quad \text{(R13a)}$$

$$\rightarrow H_2 + 2\text{-}C_7H_{15} \quad \text{(R13b)}$$

$$\rightarrow H_2 + 3\text{-}C_7H_{15} \quad \text{(R13c)}$$

$$\rightarrow H_2 + 4\text{-}C_7H_{15} \quad \text{(R13d)}$$

$$H + n\text{-}C_8H_{18} \rightarrow H_2 + 1\text{-}C_8H_{17} \quad \text{(R14a)}$$

$$\rightarrow H_2 + 2\text{-}C_8H_{17} \quad \text{(R14b)}$$

$$\rightarrow H_2 + 3\text{-}C_8H_{17} \quad \text{(R14c)}$$

$$\rightarrow H_2 + 4\text{-}C_8H_{17} \quad \text{(R14d)}$$

$$H + CH_3CH{=}CH_2 \rightarrow H_2 + CH_2CH{=}CH_2 \quad \text{(R15)}$$

$$H + CH_3CH{=}C{=}CH_2 \rightarrow H_2 + CH_2CH{=}C{=}CH_2 \quad \text{(R16)}$$

$$H + CH_3C_6H_5 \rightarrow H_2 + CH_2C_6H_5 \quad \text{(R17)}$$

$$H + CH_3CH_2CH{=}CH_2 \rightarrow H_2 + CH_3CHCH{=}CH_2 \quad \text{(R18)}$$

$$H + (CH_3)_2C{=}CH_2 \rightarrow H_2 + CH_2C(CH_3){=}CH_2 \quad \text{(R19)}$$

$$H + \text{E-}CH_3CH{=}CHCH_3 \rightarrow H_2 + \text{E-}CH_2CH{=}CHCH_3 \quad \text{(R20)}$$

$$H + \text{Z-}CH_3CH{=}CHCH_3 \rightarrow H_2 + \text{Z-}CH_2CH{=}CHCH_3 \quad \text{(R21)}$$

$$H + CH_3CH_2CH_2CH{=}CH_2 \rightarrow H_2 + CH_3CH_2CHCH{=}CH_2 \quad \text{(R22)}$$

$$H + (CH_3)_2CHCH{=}CH_2 \rightarrow H_2 + (CH_3)_2CCH{=}CH_2 \quad \text{(R23)}$$

II. Methodology

A. Reaction Class Transition State Theory (RC-TST). Within the transition state theory framework,[25] thermal rate constants of a reaction can be expressed as

$$k(T) = \kappa(T)\sigma\frac{k_B T}{h}\frac{Q^{\ddagger}(T)}{\Phi^{R}(T)}e^{\{-\Delta V^{\ddagger}/kBT\}} \quad (1)$$

where κ is the transmission coefficient accounting for the quantum mechanical tunneling effects, σ is the reaction symmetry number, $Q^{\ddagger}$ is the total partition function of the transition state, Φ^{R} is the total partition functions (per unit volume) of the reactants, $\Delta V^{\ddagger}$ is the classical barrier height, T is the temperature, and k_B and h are the Boltzmann and Planck constants, respectively.

For reactions in a given class, the differences in the rate constants of two reactions mainly come from the differences in the interactions between the reactive moiety and their substituents. Within the RC-TST framework, the rate constants of an arbitrary reaction (denoted as R_a) in a given reaction class, $k_a(T)$, is proportional to rate constants of the principal reaction (denoted as R_p) of the class, $k_p(T)$ by a temperature-dependent function $f(T)$:

$$k_a(T) = f(T)k_p(T) \quad (2)$$

Because of its small size, rate constants of the principal reaction can be calculated from first-principles using an accurate dynamical theory with potential energy information computed from a sufficiently high level of electronic structure theory. However, the rate constants of the principal reaction can also

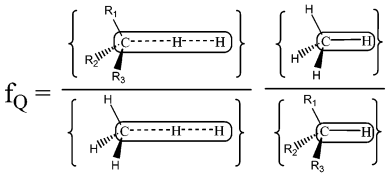

Figure 1. Schematic illustration of the factor of partition function f_Q. Brackets denote the vibrational partition functions of the species inside. The left-hand side ratio is from the transition states having the same reactive moiety C- -H- -H, and the other ratio is from the reactants having the same reactive moiety component C−H.

taken from accurate experiments if available. The key idea of the RC-TST method is to factor $f(T)$ into different components:[20]

$$f(T) = f_\kappa f_\sigma f_Q f_V \tag{3}$$

where f_κ, f_σ, f_Q, and f_V are tunneling, symmetry number, partition function and potential energy factors, respectively. These factors are simply the ratio of the corresponding components in the TST expression (see eq 1) for the two reactions:

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

$$f_\sigma = \sigma_a/\sigma_p \tag{5}$$

$$f_Q(T) = \frac{\left(\frac{Q_a^\ddagger(T)}{\Phi_a^R(T)}\right)}{\left(\frac{Q_p^\ddagger(T)}{\Phi_p^R(T)}\right)} = \frac{\left(\frac{Q_a^\ddagger(T)}{Q_p^\ddagger(T)}\right)}{\left(\frac{\Phi_a^R(T)}{\Phi_p^R(T)}\right)} \tag{6}$$

$$f_V(T) = \exp\left\{-\frac{(\Delta V_a^\ddagger - \Delta V_p^\ddagger)}{k_B T}\right\} = \exp\left\{-\frac{\Delta\Delta V^\ddagger}{k_B T}\right\} \tag{7}$$

The principle task is to determine these factors linking the rate constants of R_p and those of R_a in the same class without having to calculate k_a(T) explicitly. A detailed discussion of these factors can be found in our previous work,[20] we only provide a brief overview below.

The symmetry number factor f_σ can be determined exactly from the symmetry numbers of R_p and R_a. The symmetry number of a reaction can be easily calculated from the rotational symmetry numbers of the reactant and transition state.[26,27]

The tunneling factor f_κ is the ratio of transmission coefficients of R_a and that of R_p. Although absolute transmission coefficients for hydrogen abstraction reactions often require multidimensional tunneling methods to account for the large corner-cutting effects, because of cancellation of errors in our previous study, we have shown that the tunneling factor f_κ can be accurately predicted using the 1-D Eckart method.[28]

The partition function factor f_Q is the ratio of partition functions of the reactants and transition states of R_a and R_p (eq 6). To have a good understanding of the properties of this factor, we illustrated eq 6 in Figure 1 for an arbitrary reaction that has three substituents (R1, R2, and R3) with respect to the principal reaction. Because the total partition function is a product of translational, rotational, electronic, and vibrational partition functions and due to the specific forms of the translational and rotational partition functions, the temperature dependence of translational and rotational components of partition functions is canceled in f_Q. Furthermore, because most gas-phase reactions take place in the electronic ground state, the electronic partition functions do not contribute to f_Q. Thus, the temperature dependence of f_Q comes solely from the vibrational component. Furthermore, one can see from Figure 1 that the contributions to the vibrational partition functions from the principal components of the reactive moiety and of the substituents are canceled. Therefore, the main factors that govern the temperature dependence of the f_Q factor are the differences in the vibrational frequencies due to the coupling of substituents with the reactive moiety. Thus, even in flexible molecules where it is difficult to calculate accurately the partition functions of the low-frequency vibrational modes such as hindered rotations, their principal components are canceled in f_Q. The goal here is to establish an approximate expression of f_Q for all reactions in a given class from a small number of reactions in such a class. The potential energy factor f_V in eq 7 represents the difference of substituent effects on the classical reaction barriers of R_a and R_p. In previous studies, we have shown that this differential reaction barrier, $\Delta\Delta V^\ddagger$, can be calculated from a relatively low level of theory even though absolute reaction barriers require a much higher level of theory to achieve the acceptable level of accuracy.[21,22] In this study, we show that the classical barrier height for any reaction in the class can also be estimated from a linear energy relationship (LER) between the classical barrier height and the reaction energy with a relatively high level of accuracy. In this case, only the reaction energy is needed to calculate the rate constant for any reaction in the class. The present methodology is denoted as RC-TST/LER.

Although both the RC-TST/LER method and the group additivity (GA) method developed by Green and co-workers based on the TST framework and utilized the same reaction class concept, there are inherent differences in the methodology for obtaining thermal rate constants. The RC-TST/LER method takes advantages of the similarities in the potential surfaces of reactions in the same class to achieve cancellations in obtaining the *relative* rate constants. The thermal rate constant of any reaction in the class can be calculated from its reaction energy and the rate constants of the principal reaction. The rate constants of the principal reaction are often calculated at a much more accurate level of dynamical theory than the simple TST method, such as the canonical variational TST method augmented by the multidimensional semiclassical small curvature tunneling approximation (CVT/SCT) used in this study. Thus, one can think of the RC-TST/LER method as a procedure for extrapolating CVT/SCT rate constants of the principal reaction to rate constants of any reaction in the class. The GA method on the other hand takes advantage of the similarity in the reactive moiety of reactions in the same class to define a "supergroup" for the transition states. It then derives its group contributions to thermodynamic properties of the transition states from fitting to TST/Wigner rate constants for a selected set of reactions. The GA method can calculate *absolute* thermal rate constants without requiring any further information. In other words, the GA method is a parametrization procedure of the TST/Wigner method for a specific reaction class. Within the TST framework for the absolute rate constants, difficulties in obtaining accurate vibrational partition functions for low-frequency modes sometimes persist in the GA method.

B. Electronic Structure Calculations. The electronic structure calculations for the principal reaction (R1) have been done in detail at a variety of levels of theory.[8−11] We do not discuss it further here. For all other reactions, geometries of the reactants, transition states, and products were optimized at the BH&HLYP[29] level of theory with the cc-pVDZ basis set.[30]

Frequencies of the stationary points were also calculated at the BH&HLYP/cc-pvdz level of theory for those reactions where the partition function factors f_Q were explicitly calculated. The BH&HLYP method has been found previously to be sufficiently accurate for predicting the transtion state properties for hydrogen abstraction reactions by a radical.[31−33] The reaction barrier heights of all of the reactions were refined using the IMOMO approach[21,22] within the reaction class framework at the PMP4/cc-pVTZ//BH&HLYP/cc-pVDZ level of theory.[30,34] The AM1[35] method was also employed to optimize geometries of the reactants and products for all reactions in order to calculate the AM1 reaction energies for developing the LER between the barrier height and reaction energy as discussed below. All of the electronic structure calculations were done using the Gaussian 98 program.[29]

III. Results and Discussion

A. Linear Energy Relationship. It is well-known that the activation barriers can be predicted from the reaction energies by the Evans-Polanyi linear energy relationship.[36,37] However, this relationship is sometimes not accurate for different type of reactions.[38] Within the reaction class framework, because all of the reactions in the same class have the same reactive moiety, one can expect the deviation of the LER to be small. This is in fact the case as shown below. Our goal here is to establish an LER relationship between the classical barrier and the reaction energy so that one needs only the reaction energy to predict the thermal rate constants for any reaction in the class without having to determine the transition state structure, energy, and frequencies. It is known that in order to obtain accurate classical barrier heights a rather high level of electronic structure theory is required. On the other hand, reaction energies can be predicted at a relatively lower level of theory, such as density functional theory or even semiempirical molecular orbital theory. In our previous studies,[21,22] we have shown that one can combine the reaction class concept with the IMOMO method to predict accurate classical barriers at a reasonable computational cost. In fact, we have shown that for many reactions in the reaction class considered here the IMOMO (PMP4/cc-pVTZ: BH&HLYP/cc-pVDZ) level yields errors of less than 1 kcal/mol compared to the full PMP4/cc-pVTZ results. To develop the LER for this reaction class, we first fitted the IMOMO (PMP4: BH&HLYP) barrier heights as a function of the BH&HLYP reaction energies. We found that hydrogen abstraction reactions of alkanes and alkenes required two separate linear equations, namely

$$\Delta V^{\ddagger} = 0.6926\Delta E + 12.703 \quad (8)$$

for alkanes and

$$\Delta V^{\ddagger} = 0.3232\Delta E + 13.662 \quad (9)$$

for alkenes that form resonant stabilized transition states and radicals. The standard deviations for the two fittings are 0.34 and 0.88 kcal/mol, respectively. However, only one LER was needed to fit the barriers to the AM1 reaction energies, namely

$$\Delta V^{\ddagger} = 0.3625\Delta E + 20.602 \quad (10)$$

with the standard deviation of 0.79 kcal/mol.

Figures 2 and 3 show the linear energy relationships between reaction barrier heights calculated at the IMOMO (PMP4/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 calculations are listed in Table 1 together with experimental reaction energies of some reactions that are calculated from available experimental standard heats of formation of products and reactants. It can be seen that the absolute deviations of reaction barrier heights between LERs and full quantum calculations are smaller than 1 kcal/mol for all reactions. The mean absolute deviations of reaction barrier heights predicted from BH&HLYP reaction energies are 0.25 and 0.28 kcal/mol for reactions of alkanes and alkenes, respectively. The mean absolute deviation of reaction barrier heights predicted from the AM1 reaction energy is 0.37 kcal/mol for all reactions. These deviations are in fact smaller than the systematic errors of the computed reaction barriers from full electronic structure calculations. Thus, eqs 8−10 are expected to give good estimations of reaction barrier heights for the whole reaction class. It can also be seen from Table 1 that reaction energies predicted using the BH&HLYP/cc-pVDZ method are in good agreement with experimental data. Because the AM1 method systematically underestimates the heat of formations of hydrocarbon radicals, the predicted reaction energies are much lower than experimental data. However, this systematic error covers up the differences in the reaction

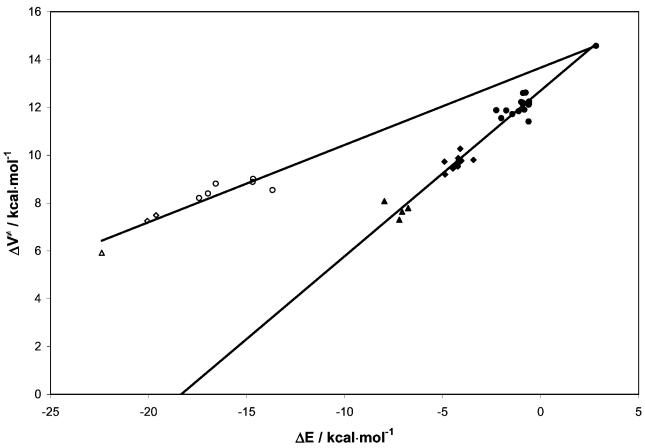

Figure 2. Linear energy relationship plots of barrier heights $\Delta V^{\ddagger}$ versus reaction energies ΔE. Barrier heights were calculated at the IMOMO-(PMP4/cc-pVTZ: BH&HLYP/cc-pVDZ) level of theory. ΔE's were calculated at the BH&HLYP/cc-pVDZ) level of theory. The filled symbols are for hydrogen abstract reactions of alkanes; the hollow symbols are for those of alkenes. The round symbols are for abstract reactions on primary carbons; the diamond symbols are for those on secondary reactions; and the triangle symbols are for those on tertiary carbons.

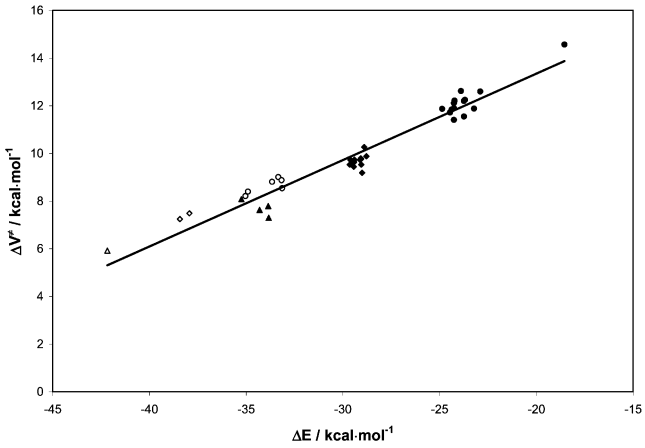

Figure 3. Same as in Figure 2, except that the reaction energies are calculated at the AM1 level of theory.

TABLE 1: Reaction Energies, Classical Barrier Heights, and Absolute Deviations between the Calculated Barrier Heights from ab Initio Calculations and from the LER Expressions with Energies in kcal/mol

	ΔE			$\Delta V^{\ddagger}$			$\lvert\Delta V^{\ddagger} - \Delta V^{\ddagger}_{LER}\rvert$	
react.	expt.[a]	DFT[b]	AM1	IMOMO[c]	DFT[b]	AM1	DFT[d]	AM1[e]
R1	0.55	2.83	−18.55	14.57	14.66	13.88	0.09	0.69
R2	−3.63	−1.12	−24.38	11.84	11.93	11.76	0.09	0.08
R3a	−3.18	−0.87	−24.24	12.17	12.10	11.82	0.07	0.36
R3b	−5.57	−4.39	−29.65	9.53	9.66	9.85	0.13	0.32
R4a		−0.91	−24.26	12.14	12.07	11.81	0.07	0.33
R4b	−5.23	−4.18	−29.41	9.74	9.81	9.94	0.07	0.20
R5a	−3.30	−0.59	−23.69	12.25	12.29	12.01	0.04	0.24
R5b	−8.56	−7.07	−34.31	7.63	7.81	8.16	0.18	0.54
R6a		−0.83	−24.26	11.90	12.13	11.81	0.23	0.09
R6b		−4.47	−29.44	9.44	9.61	9.93	0.17	0.49
R6c		−4.22	−29.05	9.53	9.78	10.07	0.25	0.54
R7		−0.90	−22.90	12.60	12.08	12.30	0.52	0.30
R8a		−1.44	−24.46	11.72	11.70	11.74	0.01	0.02
R8b		−2.01	−23.74	11.55	11.31	12.00	0.24	0.45
R8c		−4.87	−29.01	9.19	9.33	10.08	0.14	0.90
R8d	−8.68	−7.21	−33.84	7.30	7.71	8.34	0.41	0.97
R9a		−0.59	−24.26	12.14	12.29	11.81	0.15	0.33
R9b		−4.22	−29.43	9.65	9.78	9.93	0.13	0.28
R9c		−3.43	−29.08	9.80	10.33	10.06	0.53	0.26
R10a		−0.76	−23.90	12.62	12.18	11.94	0.44	0.68
R10b		−2.26	−23.22	11.88	11.14	12.18	0.74	0.31
R10c		−4.10	−28.90	10.27	9.86	10.12	0.41	0.14
R11a		−1.75	−24.87	11.87	11.49	11.59	0.38	0.28
R11b		−7.97	−35.25	8.08	7.18	7.82	0.90	0.26
R12a		−0.92	−23.75	12.20	12.06	11.99	0.13	0.21
R12b		−4.21	−28.79	9.88	9.79	10.16	0.09	0.29
R12c		−4.90	−29.62	9.73	9.31	9.86	0.42	0.14
R12d		−6.76	−33.86	7.79	8.02	8.33	0.23	0.54
R12e		−0.99	−24.23	12.22	12.02	11.82	0.20	0.40
R13a		−0.61	−24.26	12.11	12.28	11.81	0.17	0.30
R13b		−4.23	−29.43	9.63	9.77	9.93	0.14	0.30
R13c		−4.12	−29.11	9.73	9.85	10.05	0.12	0.32
R13d		−4.05	−29.07	9.77	9.90	10.06	0.13	0.29
R14a		−0.61	−24.26	11.41	12.28	11.81	0.87	0.40
R14b		−4.24	−29.43	9.63	9.77	9.93	0.14	0.30
R14c		−4.11	−29.10	9.76	9.86	10.05	0.10	0.29
R14d		−4.05	−29.07	9.76	9.90	10.06	0.14	0.30
MAD							0.25[f]	
R15	−16.11	−16.57	−33.66	8.81	8.31	8.40	0.50	0.41
R16		−14.67	−33.34	9.01	8.92	8.52	0.09	0.49
R17	−14.58	−13.68	−33.14	8.54	9.24	8.59	0.70	0.05
R18		−20.07	−38.43	7.25	7.18	6.67	0.08	0.58
R19		−14.69	−33.17	8.88	8.91	8.58	0.03	0.30
R20		−16.97	−34.91	8.4	8.18	7.95	0.22	0.45
R21		−17.42	−35.04	8.21	8.03	7.90	0.18	0.31
R22		−19.62	−37.94	7.49	7.32	6.85	0.17	0.64
R23		−22.39	−42.18	5.92	6.42	5.31	0.50	0.61
MAD							0.28[g]	0.37[h]

[a] Calculated from standard heat of formation of products and reactants from NIST database. [b] Calculated at the BH&HLYP/cc-pVDZ level of theory. [c] Calculated at the IMOMO (PMP4/cc-pVTZ//BH&HLYP/cc-pVDZ) level of theory. [d] $\Delta V^{\ddagger}_{LER}$ was calculated from the LERs for BH&HLYP reaction energies. [e] $\Delta V^{\ddagger}_{LER}$ was calculated from the LER for AM1 reaction energies. [f] Mean absolute deviations (MAD) for reactions R1 ∼ R14d. [g] Mean absolute deviations for reactions R15 ∼ R23. [h] Mean absolute deviations for all reactions.

energies of the two sub-groups, abstraction of alkanes and alkenes and thus yields a single LER expression without a significant increase of error. It is important to point out that the LER expressions developed here were for alkanes and selected alkenes and may not be applicable for other substituted hydrocarbons.

B. Reaction Symmetry Number Factor. The symmetry number factors were simply calculated from the ratio of symmetry numbers of target and principal reactions as listed in Table 2.

C. Tunneling Factor. The tunneling factor f_κ is the ratio of tunneling coefficients of the target and principal reactions. We use the Eckart tunneling method[28] to calculate the tunneling coefficients. This method requires only the imaginary frequency and forward and reverse barrier heights of a reaction. The imaginary frequency of 1307 cm^{-1} of the principal reaction calculated at the BH&HLYP/cc-pVDZ level of theory was assumed for all reactions because of its small variation found previously for different reactions in this class.[20] Table 2 shows calculated tunneling factors of the reactions listed above using the barrier heights calculated from the two LER expressions above. It can be seen that the f_κ calculated from barrier heights predicted using AM1 reaction energies are close to those predicted using BH&HLYP reaction barriers with the largest deviation at about 13% (R23) and normal deviations of less than 10%. These deviations mainly come from the overestimation of the reverse barriers by the AM1 method. Because almost all of the reactions in this class are exothermic (except for the principal reaction), the forward barriers heights dominate the quantum transmission energy region. At a given temperature,

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

react.	f_σ	f_κ^a	f_κ^b	react.	f_σ	f_κ^a	f_κ^b
R1	(4)[c]	(8.21)	(8.21)	R11b	0.50	0.83	0.83
R2	1.50	0.98	1.04	R12a	0.75	0.98	1.05
R3a	1.50	0.99	1.05	R12b	0.50	0.94	0.96
R3b	0.50	0.94	0.95	R12c	0.50	0.92	0.95
R4a	1.50	0.99	1.04	R12d	0.25	0.87	0.87
R4b	1.00	0.94	0.95	R12e	1.50	0.98	1.04
R5a	2.25	0.99	1.05	R13a	1.50	0.99	1.04
R5b	0.25	0.86	0.85	R13b	1.00	0.94	0.95
R6a	1.50	0.99	1.04	R13c	1.00	0.94	0.96
R6b	1.00	0.94	0.95	R13d	0.50	0.94	0.96
R6c	0.50	0.94	0.96	R14a	1.50	0.99	1.04
R7	3.00	0.99	1.06	R14b	1.00	0.94	0.95
R8a	0.75	0.98	1.05	R14c	1.00	0.94	0.96
R8b	1.50	0.98	1.05	R14d	1.00	0.94	0.96
R8c	0.50	0.92	0.96	R15	0.75	0.88	0.87
R8d	0.25	0.86	0.86	R16	0.75	0.92	0.87
R9a	1.50	0.99	1.05	R17	0.75	0.93	0.88
R9b	1.00	0.94	0.95	R18	0.50	0.81	0.76
R9c	1.00	0.95	0.96	R19	1.50	0.92	0.87
R10a	0.75	0.99	1.05	R20	0.75	0.87	0.84
R10b	2.25	0.97	1.06	R21	0.75	0.87	0.84
R10c	0.50	0.94	0.96	R22	0.50	0.82	0.77
R11a	3.00	0.98	1.04	R23	0.25	0.76	0.66

[a] Using the Eckart model with the forward barrier heights predicted from the LER at the IMOMO (PMP4/cc-pVTZ//BH&HLYP/cc-pVDZ) level of theory by substituting the reaction energies at the BH&HLYP/cc-pVDZ level of theory into eqs 8−9. The imaginary frequency of 1307 cm^{-1} of the principal reaction was used for all reactions. [b] Same as above, except that the forward barrier heights were predicted from the LER with AM1 reaction energies (eq 10). [c] Values in parentheses are the symmetry number and tunneling coefficients of the principal reaction.

the f_κ values of abstraction reactions from the same type of hydrogen atom (primary, secondary or tertiary) of alkanes are almost the same. Although the f_κ of hydrogen abstraction reactions of alkenes forming resonant stabilized products are about 10% smaller than those of reactions of corresponding alkanes at 300 K, the differences between them decrease rapidly as the temperature increases. For simplicity, we derived expressions for the temperature dependence of f_κ of three model reactions to approximate the f_κ value for all other reactions. The three model reactions chosen were H + C_2H_6 for abstraction from a primary carbon, H + $CH_3CH_2CH_3 \rightarrow H_2 + (CH_3)_2CH$ for abstraction from a secondary carbon, and H + $(CH_3)_3CH \rightarrow H_2 + (CH_3)_3C$ for abstraction from a tertiary carbon. The temperature dependence of f_κ of three model reactions is shown in Figure 4 and is fitted to a general expression. The fitted equations for the abstraction from primary, secondary, and tertiary carbons are

$$f_\kappa(T) = 1 - \exp(-7.861 \times 10^{-3}\, T - 2.081 \times 10^{-5}\, T^2) \quad (11)$$

$$f_\kappa(T) = 1 - \exp(5.610 \times 10^{-3}\, T - 4.675 \times 10^{-5}\, T^2) \quad (12)$$

$$f_\kappa(T) = 1 - \exp(5.678 \times 10^{-3} T - 3.641 \times 10^{-5}\, T^2) \quad (13)$$

respectively.

D. Partition Function Factor f_Q. Figure 5 shows the temperature dependence of f_Q for a number of typical reactions in the class. Only small temperature dependence in f_Q is observed at low temperatures. The f_Q of each reaction approaches a constant when the temperature increases. As mentioned in our previous study, we can make an approximation

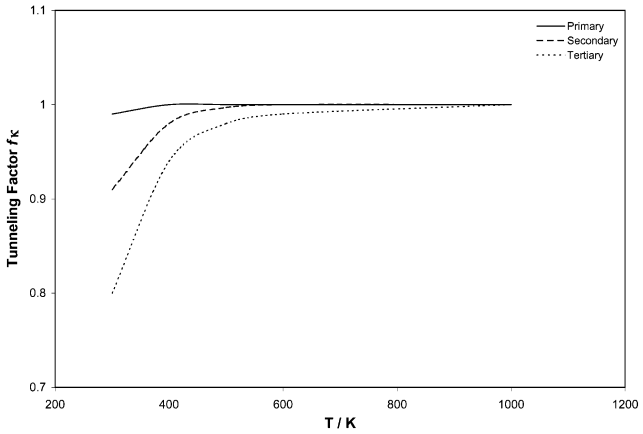

Figure 4. Plot of the tunneling factor f_κ as functions of the temperature for abstraction of of hydrogen from primary (solid line), secondary (long dashed line), and tertiary (dotted line) carbon atom.

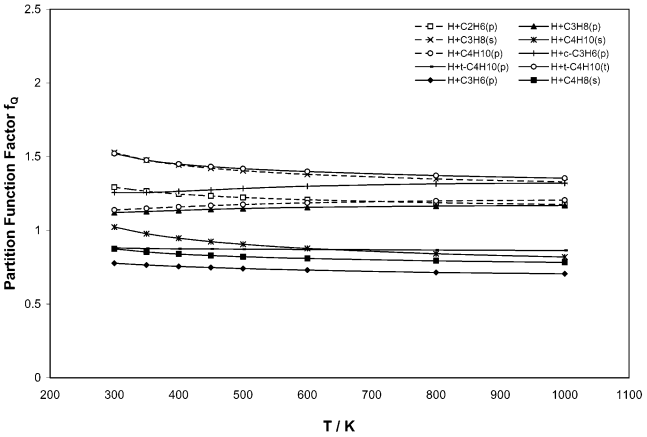

Figure 5. Plot of the partition function factor f_Q as functions of the temperature for selected hydrogen abstraction reactions of alkanes and alkenes. The letters p, s and t in parentheses are for hydrogen abstraction from primary, secondary and tertiary carbons, respectively.

that f_Q is a constant and has the high-temperature limit value (1.18) of the H + C_2H_6 reaction. This would make the largest error only about 70% in the rate constants for the temperatures above 300 K for these reactions. For the sake of simplicity, we can approximate f_Q to be unity for this reaction class. This would make the largest error of f_Q only about 40%. It is important to point out that the relatively small temperature dependence of the H + H−C(sp^3) reaction class may not be a general observation. We should be able to gain more insight into the temperature dependence of f_Q when the theory is applied to different types of reaction classes. This is being considered in our lab.

E. Rate Constants of the Principal Reaction H + CH_4. Rate constants of the principal reaction H + $CH_4 \rightarrow H_2 + CH_3$ were taken from our previous direct ab initio dynamics study[9] using a full canonical variational TST with multi-dimensional semiclassical small-curvature tunneling (CVT/SCT) calculations. The potential energy surface information was calculated at the PMP4/cc-pVTZ//BH&HLYP/cc-pVDZ level of theory; that is, geometries and frequencies at the stationary points and along the minimum energy path were calculated at the BH&HLYP/cc-pVDZ level, whereas energetic information was then corrected by single-point energy calculations at the PMP4/cc-pVTZ level of theory. The predicted rate constants were in excellent agreement with experimental data. More details on the calculations can be found elsewhere.[9] For convenience in the application of RC-TST, we have fitted the calculated rate constants

TABLE 3: Ab Initio Derived Parameters and Formulations of the RC-TST/LER Method for the H + H−C(sp^3) Hydrogen Abstraction Reaction Class

$$k(T) = f_\sigma f_\kappa(T) f_Q(T) f_v(T) k_p(T)$$
$$f_V(T) = \exp\{-(\Delta V^\ddagger - \Delta V_p^\ddagger)/k_B T\}$$

f_σ	(see Table 2 for examples)
$f_\kappa(T)$	$1 - \exp(-7.861 \times 10^{-3}\, T - 2.081 \times 10^{-5}\, T^2)$ for primary carbon $1 - \exp(5.610 \times 10^{-3}\, T - 4.675 \times 10^{-5}\, T^2)$ for secondary carbon $1 - \exp(5.678 \times 10^{-3}\, T - 3.641 \times 10^{-5}\, T^2)$ for tertiary carbon
f_Q	1.0
$\Delta V^\ddagger$ (kcal/mol)	$(0.6926\Delta E + 12.703)$ for alkanes, ΔE at the BH&HLYP/cc-pVDZ level $(0.3232\Delta E + 13.662)$ for alkenes, ΔE at the BH&HLYP/cc-pVDZ level $(0.3625\Delta E + 20.602)$ for all types, ΔE at the AM1 level
$\Delta V_p^\ddagger$ (kcal/mol)	14.57
$k_p(T)$	$6.42 \times 10^{-26}\, T^{4.71} \exp(-3127.41/T)$ (cm^3 molecule^{-1} s^{-1})

for the H + CH_4 reaction to an Arrhenius expression and obtained

$$k_p = 6.42 \times 10^{-26}\, T^{4.71}\, e^{(-3127.41/T)}\ (\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}) \quad (14)$$

F. Predictions of Rate Constants. What we have established so far are all necessary parameters for application of the RC-TST theory to predict rate constants for any reaction in the H + H−C(sp^3) class. Only the reaction energy is needed, and it can be calculated at either the BH&HLYP/cc-pVDZ or the AM1 levels of theory. Table 3 summarizes the RC-TST parameters for this reaction class. We selected several reactions whose rate constants have been determined experimentally or derived from other experimental data for more detailed discussion to illustrate the theory.

Figure 6a−c shows the Arrhenius plots of the primary, secondary, and total hydrogen abstraction reactions of C_3H_8, respectively. The predicted total rate constants by the RC-TST/LER method are in excellent agreement with experimental measurements.[18,39−44] Although there is no direct experimental data for the primary and secondary hydrogen abstraction reactions, our calculated values are also very close to rate constants derived from other experimental data.[17,18,45−47] Furthermore, there are no significant differences in the rate constants calculated using AM1 reaction energies with those using BH&HLYP reaction energies.

As shown in previous sections, the barrier heights, tunneling factors, and partition function factors of the hydrogen abstraction reaction of alkenes that form resonant stabilized products can be estimated well in the same reaction class with the hydrogen abstraction reaction of alkanes. Although there is very limited direct measurements of rate constants for these types of reactions, Figure 7 shows the predicted rate constants of the reaction R15 using the RC-TST method and the experimental derived data.[48,49] The RC-TST/LER method again yields reasonably good prediction of the rate constants.

To determine the overall efficiency of the RC-TST method, we performed three different analyses. One is to compare the calculated rate constants of the reactions with those from direct measurements or derived from other experimental data. Because experimental data for each reaction have different levels of uncertainty, the differences between the calculated and experimental data cannot provide a good measure on the accuracy of the RC-TST method. Such comparisons can only give semiquantitative indications of its accuracy. As mentioned earlier, the RC-TST/LER methodology can be thought of as a procedure for extrapolating CVT/SCT rate constants of the principal reaction to those of any given reaction in the class. Thus, the ideal analysis would be to compare the results of the RC-TST/LER method to those from full CVT/SCT calculations using

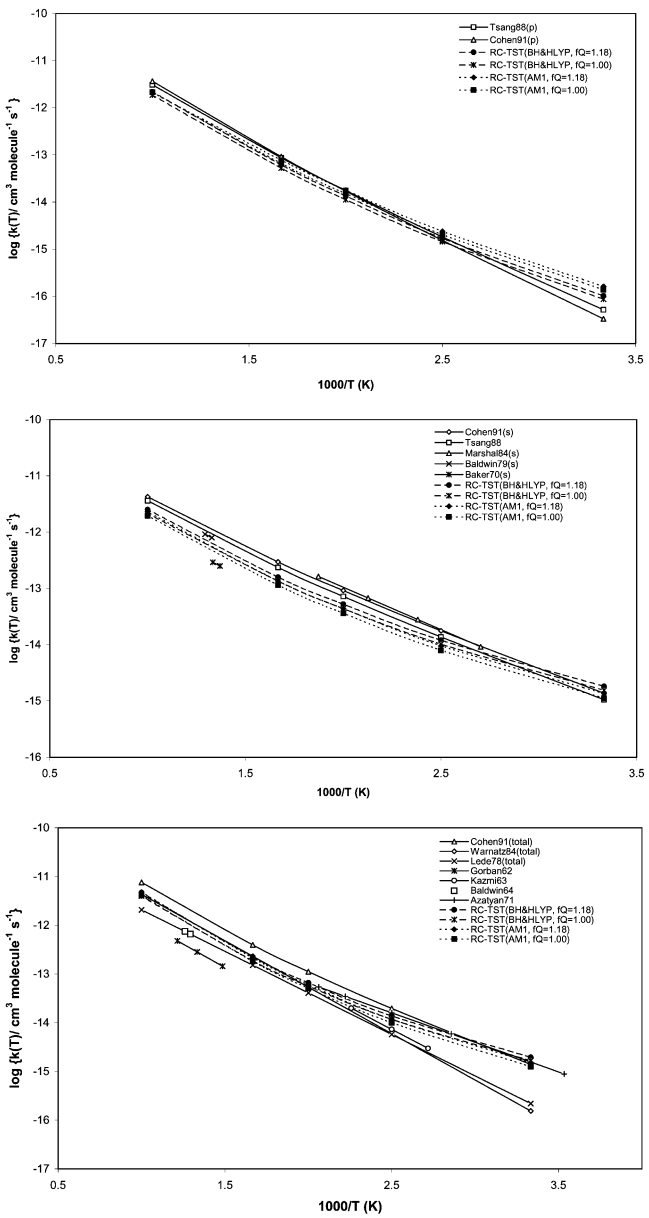

Figure 6. Arrhenius plots of the calculated rate constants using the RC-TST/LER method for the H + C_3H_8 reaction along with available experimental data: (a) For the hydrogen abstraction from the primary carbon (reaction R3a); (b) from the secondary carbon (R3b); (c) for the total hydrogen abstraction. BH&HLYP denotes that the LER was used with the BH&HLYP reaction energies and similarly AM1 denotes that the AM1 reaction energies were used. $f_Q = 1.18$ and $f_Q = 1.00$ are the values of partition function factors employed in the calculations. The experimental data are taken from the papers in the reference section indicated by the first author and year.

TABLE 4: Comparison between the Predicted RC-TST/LER Rate Constants (cm^3 $molecule^{-1}$ s^{-1}) and Available Experimental Data for Selected Reactions

react.	T(K)[a]	k_{expt}[b]	ref	$k_{BH\&HLYP}$[c]	% deviation	k_{AM1}[d]	% deviation
R2	1000	1.82×10^{-12}	50	2.04×10^{-12}	12%	2.22×10^{-12}	22%
R3a	1000	3.06×10^{-12}	45	1.87×10^{-12}	39%	2.15×10^{-12}	30%
R3b	1000	3.60×10^{-12}	45	2.13×10^{-12}	41%	1.94×10^{-12}	46%
R4a	750	4.08×10^{-13}	17	2.90×10^{-13}	29%	3.45×10^{-13}	15%
R4b	750	1.26×10^{-12}	17	8.80×10^{-13}	30%	8.07×10^{-13}	36%
R5a	1000	4.17×10^{-12}	51	2.56×10^{-12}	39%	2.94×10^{-12}	29%
R5b	1000	4.32×10^{-12}	51	2.70×10^{-12}	38%	2.26×10^{-12}	48%
R6a	750	4.08×10^{-13}	17	2.78×10^{-13}	32%	3.45×10^{-13}	15%
R6b	750	1.56×10^{-12}	17	1.01×10^{-12}	35%	8.12×10^{-13}	48%
R7	750	8.17×10^{-13}	17	5.76×10^{-13}	29%	4.97×10^{-13}	39%
R8a	750	2.05×10^{-13}	17	1.86×10^{-13}	9%	1.81×10^{-13}	12%
R8c	750	7.82×10^{-13}	17	6.07×10^{-13}	22%	3.67×10^{-13}	53%
R8d	750	1.49×10^{-12}	17	9.01×10^{-13}	40%	5.90×10^{-13}	60%
R15	1000	2.55×10^{-12}	49	6.30×10^{-12}	147%	6.04×10^{-12}	137%
R17	1000	2.88×10^{-12}	52	3.95×10^{-12}	37%	5.47×10^{-12}	90%
R19	1000	5.11×10^{-12}	53	9.32×10^{-12}	82%	1.10×10^{-11}	115%
average					42%		51%

[a] Temperatures where the experimental data are available. [b] Direct measurement or derived from other experimental data. [c] Using BH&HLYP reaction energies. [d] Using AM1 reaction energies.

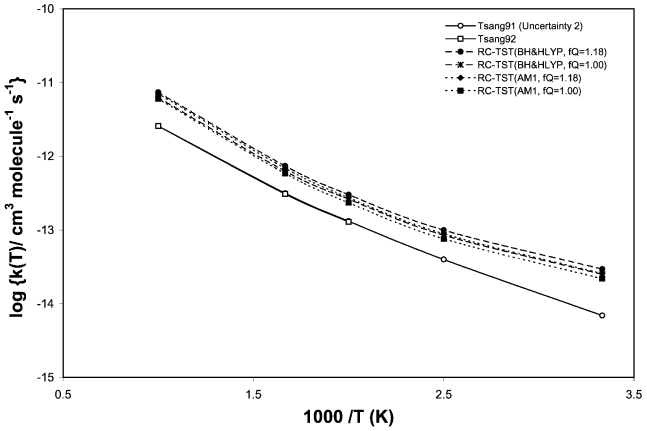

Figure 7. Same as in Figure 6, except for the H + C_3H_6 reaction.

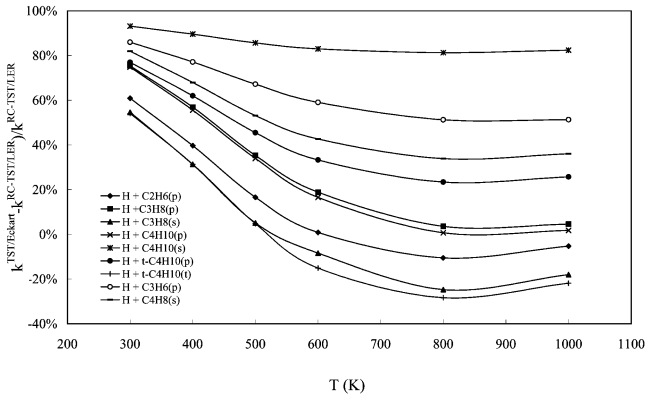

Figure 8. Relative deviations as functions of the temperature between rate constants calculated from the RC-TST/LER and full TST/Eckart methods.

the same level of electronic structure theory as used for the principal reaction. Unfortunately, such an analysis is beyond our computational capability at the present time. Alternatively, we provide an analysis that is not as rigorous but still quite useful. Accordingly, we compared the calculated rate constants for a small number of reactions using both the RC-TST/LER and full TST/Eckart methods in the second analysis. Finally, we examined the errors in different factors in the RC-TST/LER method in the third analysis. In particular, errors in f_κ resulted from the use of the approximate functions, which depend only on the type of the abstracting hydrogen. Errors in f_Q resulted from using a constant for all reactions in the class. Errors in f_V resulted from using the LER expressions to calculate the barrier heights.

The comparison between calculated and experimental results is listed in Table 4. Because of the limitation in the temperature range of available experimental data, we calculated rate constants at either 750 or 1000 K. We can see that the mean absolute deviation of rate constants calculated from the RC-TST/LER-(BH&HLYP), using the BH&HLYP reaction energies, is only 42% compared with experimental data. The mean absolute deviation of rate constants calculated from the RC-TST/LER-(AM1), using the AM1 reaction energies, is only 9% higher than that from the RC-TST/LER(BH&HLYP). These deviations in fact fall within the systematic uncertainty of the measurements of the experiments. The deviations of rate constants of hydrogen abstraction reactions of alkenes that form resonant stabilized products are larger than those from reactions of alkanes. This is because the principal H + CH_4 reaction does not have the resonance stabilization effects on the transition states. However, for simplicity and practicality, we neglected such effects and found that the deviations of rate constants are still within an acceptable level of accuracy.

The results for the second analysis (i.e., the comparisons between the RC-TST/LER and full TST/Eckart methods) are shown in Figure 8. Here we plotted the relative deviation defined by $(|k^{TST/Eckart} - k^{RC-TST/LER}|/k^{RC-TST/LER})$ percent versus the temperature for several selected reactions. The relative errors are less than 100% for all test cases. This is certainly an acceptable level of accuracy for reaction engineering purposes. Only a small difference was found for the relative errors between hydrogen abstraction reactions on alkanes and alkenes. Recall that the RC-TST/LER is an extrapolation of the CVT/SCT method, not the TST/Eckart method. Thus, one can expect larger differences when comparing the RC-TST/LER results to those from the full TST/Eckart. A more precise analysis would be to examine the systematic errors arising from approximations used in the RC-TST/LER method as discussed below.

The results of the analysis on the errors from different relative rate factors, namely f_κ, f_Q, and f_V used in the RC-TST/LER method are shown in Figure 9. In this figure, we plotted the absolute errors averaged over a number of selected reactions as functions of temperature. For f_κ and f_V, the average was taken from all reactions considered, whereas that for f_Q was taken

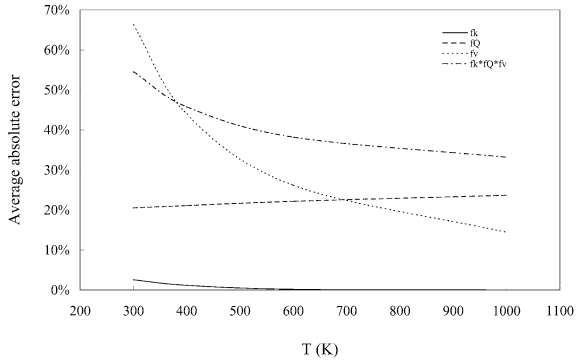

Figure 9. Average absolute errors of the total relative rate factor $f(T)$ (eq 3) and its components, namely the tunneling (f_κ), partition (f_Q), and potential (f_V) factors as functions of the temperature.

only from the 10 reactions shown in Figure 5. Errors from all components are less than 70% for the temperature range from 300 to 1000 K. The errors from the f_V factor show the largest temperature dependence and decrease as the temperature increases. The total errors in the relative rate factors are less than 55% and decrease as the temperature increases. These are systematic errors of the RC-TST/LER method that can be compared with the relative errors between the TST/Wigner and group additivity results reported by Green et al.[23] because the group additivity parameters were derived from the TST/Wigner results. We found that both methods have a similar magnitude of systematic errors. The main difference is that the RC-TST/LER method approximates the full CVT/SCT level of theory, whereas the GA method approximates only the TST/Wigner level. For hydrogen abstraction reactions, it is well-known that the multidimensional semiclassical small curvature tunneling (SCT) method is much more accurate for predicting the tunneling probability than the simple Wigner expression.

IV. Conclusion

We have presented an application of the reaction class transition state theory in conjunction with the linear energy relationship (RC-TST/LER) for prediction of thermal rate constants of the reaction class $H + H-C(sp^3)$ that involves both hydrogen abstraction from alkanes and alkenes, which in turn form resonant stabilized products. The RC-TST/LER method is shown to be both simple and effective for predicting rate constants of any reaction in a given class from only the reaction energy that can be calculated either at the BH&HLYP or AM1 level of theory. We have tested the ab initio derived parameters for the RC-TST/LER method for the above reaction class by predicting rate constants for 46 reactions where some experimental data was also available. We found that the predicted rate constants are in good agreement with experimental data. The mean absolute deviations of rate constants calculated using the BH&HLYP and AM1 reaction energies respectively are only 42% and 51% compared to the available experimental data. We have also found that the RC-TST/LER method predicts rate constants within the factor of 2 compared to the results from full TST/Eckart calculations though the later requires much more computational resources. Finally, detailed analysis shows that the systematic errors in the calculated rate constants arise from approximations used in the RC-TST/LER method are less than 50% and this is encouraging.

Acknowledgment. This work is supported by the University of Utah Center for the Simulation of Accidental Fires & Explosions, funded by the Department of Energy, Lawrence Livermore National Laboratory, under Subcontract B341493, and a generous gift from the Dow Chemical Company. The authors thank the Utah Center for High Performance Computing for computer time support.

References and Notes

(1) Bryukov, M. G.; Slagle, I. R.; Knyazev, V. D. *J. Phys. Chem. A* **2001**, *105*, 6900.
(2) Azatyan, V. V.; Gazaryan, K. G.; Garibyan, T. A. *Kinet. Katal.* **1988**, *29*, 38.
(3) Sutherland, J. W.; Su, M.-C.; Michael, J. V. *Int. J. Chem. Kinet.* **2001**, *33*, 669.
(4) Cao, J.-R.; Back, M. H. *Can. J. Chem.* **1984**, *62*, 86.
(5) Jones, W. E.; Ma, J. L. *Can. J. Chem.* **1986**, *64*, 2192.
(6) Rabinowitz, M. J.; Sutherland, J. W.; Patterson, P. M.; Klemm, R. B. *J. Phys. Chem.* **1991**, *95*, 674.
(7) Marquaire, P.-M.; Dastidar, A. G.; Manthorne, K. C.; Pacey, P. D. *Can. J. Chem.* **1994**, *72*, 600.
(8) Huarte-Larranaga, F.; Manthe, U. *J. Phys. Chem. A* **2001**, *105*, 2522.
(9) Truong, T. N. *J. Chem. Phys.* **1994**, *100*, 14.
(10) Kraka, E.; Gauss, J.; Cremer, D. *J. Chem. Phys.* **1993**, *99*, 5306.
(11) Joseph, T.; Steckler, R.; Truhlar, D. G. *J. Chem. Phys.* **1987**, *87*, 7036.
(12) Fernandez-Ramos, A.; Martinez-Nunez, E.; Smedarchina, Z.; Vazquez, S. A. *Chem. Phys. Lett.* **2001**, *341*, 351.
(13) Loser, U.; Scherzer, K.; Weber, K. *Z. Phys. Chem.* **1989**, *270*, 237.
(14) Nicholas, J. E.; Vaghijiani, G. L. *J. Chem. Phys.* **1989**, *91*, 5121.
(15) Mebel, A. M.; Lin, M. C.; Yu, T.; Morokuma, K. *J. Phys. Chem. A* **1997**, *101*, 3189.
(16) Mebel, A. M.; Lin, M. C.; Chakraborty, D.; Park, J.; Lin, S. H.; Lee, Y. T. *J. Chem. Phys.* **2001**, *114*, 8421.
(17) Baldwin, R. F.; Walker, R. W. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 140.
(18) Cohen, N. *Int. J. Chem. Kinet.* **1991**, *23*, 683.
(19) Cohen, N. *Int. J. Chem. Kinet.* **1991**, *23*, 397.
(20) Truong, T. N. *J. Chem. Phys.* **2000**, *113*, 4957.
(21) Truong, T. N.; Maity, D. K.; Truong, T.-T. T. *J. Chem. Phys.* **2000**, *112*, 24.
(22) Truong, T. N.; Truong, T.-T. T. *Chem. Phys. Lett.* **1999**, *314*, 529.
(23) Sumathi, R.; Carstensen, H.-H.; Green, W. H., Jr. *J. Phys. Chem. A* **2001**, *105*, 6910.
(24) Sumathi, R.; Carstensen, H.-H.; Green, W. H., Jr. *J. Phys. Chem. A* **2001**, *105*, 8969.
(25) Truhlar, D. G.; Garrett, B. C.; Klippenstein, S. J. *J. Phys. Chem.* **1996**, *100*, 12771.
(26) Duncan, W. T.; Bell, R. L.; Truong, T. N. *J. Compt. Chem.* **1998**, *19*, 1039.
(27) Baer, T.; Hase, W. L. *Unimolecular Reaction Dynamics*; Oxford University Press: New York, 1996.
(28) Miller, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 6810.
(29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
(30) Woon, D. E.; Dunning, T. H. J. *J. Phys. Chem.* **1993**, *98*, 1358.
(31) Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 4811.
(32) Zhang, Q.; Bell, R.; Truong, T. N. *J. Phys. Chem.* **1995**, *99*, 592.
(33) Truong, T. N.; Duncan, W. **1994**, *101*, 7408.
(34) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91.
(35) Dewar, M. J. S.; Stewart, J. J. P.; Zoebisch, E. G.; Healy, E. F. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
(36) Evans, M. G.; Polanyi, M. *Proc. R. Soc. A* **1936**, *154*, 133.
(37) Polanyi, J. C. *Acc. Chem. Res.* **1972**, *5*, 161.
(38) Blowers, P.; Masel, R. *AIChE J.* **2000**, *46*, 2041.
(39) Warnatz, J. In *Combustion Chemistry*; Gardiner, W. C., Jr., Ed.; Springer-Verlag: New York, 1984.
(40) Lede, J.; Villermaux, J. *Can. J. Chem.* **1978**, *56*, 392.
(41) Azatyan, V. V.; Filippov, S. B.; Khachatryan, M. S. *Kinet. Catal.* **1971**, *12*, 1.
(42) Baldwin, R. R. *Trans. Faraday Soc.* **1964**, *60*, 527.

(43) Kazmi, H. A.; Diefendorf, R. J.; Le Roy, D. J. *Can. J. Chem.* **1963**, *41*, 690.
(44) Gorban, N. I.; Nalbandyan, A. B. *Russ. J. Phys. Chem.* **1962**, *36*, 946.
(45) Tsang, W. *J. Phys. Chem. Ref. Data* **1988**, *17*, 887.
(46) Marshall, R. M.; Purnell, H.; Sheppard, A. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 2999.
(47) Baker, R. R.; Baldwin, R. R.; Walker, R. W. *Trans. Faraday Soc.* **1970**, *66*, 2812.
(48) Tsang, W. *J. Phys. Chem. Ref. Data* **1991**, *20*, 221.
(49) Tsang, W. *Ind. Eng. Chem.* **1992**, *31*, 3.
(50) Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Esser, C.; Frank, P.; Just, T.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. *J. Phys. Chem. Ref. Data* **1992**, *21*, 411.
(51) Tsang, W. *J. Phys. Chem. Ref. Data* **1990**, *19*, 1.
(52) Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Frank, P.; Hayman, G.; Just, T.; Kerr, J. A.; Murrells, T.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. *J. Phys. Chem. Ref. Data* **1994**, *23*, 847.
(53) Tsang, W.; Walker, J. A. *Symp. Int. Combust. Proc.* **1989**, *22*, 1015.