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Reaction class transition state theory: Hydrogen abstraction reactions by hydrogen atoms as test cases

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We present a new method called Reaction Class Transition State Theory (RC-TST) for estimating thermal rate constants of a large number of reactions in a class. This method is based on the transition state theory framework within the reaction class approach. Thermal rate constants of a given reaction in a class relative to those of its principal reaction can be efficiently predicted from only its differential barrier height and reaction energy. Such requirements are much less than what is needed by the conventional TST method. Furthermore, we have shown that the differential energetic information can be calculated at a relatively low level of theory. No frequency calculation beyond those of the principal reaction is required for this theory. The new theory was applied to a number of hydrogen abstraction reactions. Excellent agreement with experimental data shows that the RC-TST method can be very useful in design of fundamental kinetic models of complex reactions. [S0021-9606(00)01133-8]

I. INTRODUCTION

One of the goals of computational science is to predict observables where experiments have not yet been done or have difficulties in carrying out. In the area of chemical kinetic theory, there has been much progress in developing direct *ab initio* dynamics methods based on the transition state theory framework for calculating rate coefficients from first principles.[1–10] These methods have achieved a rather excellent level of accuracy even for large biological systems.[11–13] It should be noted that applications of such methods are done for one chemical system at a time. Among the existing methods, the simplest and most cost effective one is the well-known transition state theory[14] (TST), which requires only structural, energetic and vibrational frequency information at the reactant and transition state. For many combustion systems, kinetic models often consist of the order of thousand of elementary reactions. There are a large number of these reactions whose kinetic parameters are not known. It is still impractical to carry out calculations of thermal rate constants for every one of such reactions even using the TST method at a sufficiently accurate level of electronic structure theory. Furthermore, in practice only a much smaller set of reactions from the detailed kinetic model is important to the combustion system under a given operating condition. To determine such a set, one only needs a good estimate of the unknown kinetic parameters to perform sensitivity analysis on the mechanism. Thus, it is much better to perform accurate rate calculations for reactions after that has been determined to be important to the mechanism.

The central task is to have a good estimate of kinetic parameters for a large number of reactions. A simple and common practice is to assign the unknown kinetic parameters by those of a similar reaction. A better approach is to employ the Evan–Polanyi linear free-energy relationship between the activation energies and bond dissociation energies or heats of reaction of similar reactions to estimate the unknown activation energy. Both approaches are empirical and have large uncertainty in the estimated rate constants. There have been some efforts to determine whether rate constants are additive so that rate constants can be estimated from separate components. However, it was proven that rate constants are not. In the case where some limited rate information is available, for instance a single rate measurement, one can use a procedure called the thermochemical kinetics TST (TK-TST) method developed by Benson and co-workers[15] and later refined by Cohen and co-workers[16–19] to extrapolate to other temperatures.

Recently, we have introduced the concept of reaction class into both electronic structure as well as dynamical calculations. This concept recognizes that all reactions in a given class have the same reactive moiety, thus they should have certain similarities on their potential surfaces along the reaction coordinate. We have shown that coupling this idea with the ONIOM methodology[20–22] leads to an efficient computational strategy for accurate determination of barrier heights and reaction energies of reactions in a class.[23] In addition, by exploring similarities on the potential surfaces of reactions in a class, we found that several features are conserved and thus can be transferred among reactions in the class. This led to the development of two new tunneling models[9,10] as approximations to the multidimensional semiclassical small curvature tunneling (SCT) (Ref. 24) method. These tunneling models have shown to be quite accurate yet they require substantially less computational demand compared to that of the SCT method. In this study, again using the reaction class concept we present a new computational methodology for calculating thermal rate coefficients for a large number of elementary reactions efficiently. This method is based on the transition state theory framework for determining relative rate constants of reactions in the class.

The focus of this study is to illustrate the theory and to test it by performing actual applications to an important class of combustion reactions, namely, the hydrogen abstraction reactions by hydrogen atoms.

II. REACTION CLASS TRANSITION STATE THEORY (RC-TST)

From the transition state theory framework,[14] thermal rate coefficient can be expressed as

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

where κ 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 reactant, respectively; $\Delta V^{\ddagger}$ is the classical barrier height; T is the temperature; k_B and h are the Boltzmann and Planck constants, respectively.

Let us consider a reaction class where all elementary reactions in the class have the same reactive moiety, with k_1 the rate coefficient of the principal reaction R1, the smallest reaction in the class, and k_2 the rate coefficient of some other reaction R2 in the same class. Due to the small size, k_1 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. Thus, k_1 can be readily available. The task is to evaluate the rate coefficient k_2.

The principle idea of the RC-TST method is to factor the ratio of the two rate constants k_2 and k_1 into different components, namely, tunneling, reaction symmetry, partition function, and potential energy, as defined below:

$$\frac{k_2}{k_1}=f_{\kappa}f_{\sigma}f_{Q}f_{V}. \tag{2}$$

By using the reaction class approach, these factors can be efficiently evaluated so that a large number of reactions in the class can be estimated from k_1 and these factors. We discuss how to approximate these factors separately below.

A. Ratio of the transmission coefficient, f_{κ}

$$f_{\kappa}(T)=\frac{\kappa_2(T)}{\kappa_1(T)}. \tag{3}$$

The transmission coefficient κ_1 of the principal reaction can be calculated from the simple Eckart model[25] or from a more accurate method such as the SCT (Ref. 24) approach. To take advantage of the possibility for cancellation of errors, both κ_1 and κ_2 in Eq. (3) should be calculated from the same tunneling model. For simplicity, we propose to use the Eckart model. However, in this study, we modified the Eckart tunneling model[25] proposed earlier to fit with the reaction class methodology. In the previous model, the Eckart function representing the zero-point energy corrected potential curve for tunneling is assumed to have the same width as of the classical potential curve. This potential width depends not only on the imaginary frequency but also on the classical barrier height and reaction energy. Since the barrier height and reaction energy vary for different reactions in a class, the potential width is not a conserved quantity. However, from analyzing transition state properties of different reactions in a class discussed below, we found the imaginary frequency is a more conserved quantity. Thus, in the RC-TST method, we assume that reactions in the class have the same imaginary frequency and zero-point energy corrections to the barrier and reaction energy as of the principal reaction, and they are used to calculate the potential for tunneling for different reactions in the class. This change introduces only a small difference in the calculated transmission coefficients at very low temperatures compared to those from the original Eckart model. Thus, for each reaction we only need the differential barrier height and reaction energy from those of the principal reaction to determine the potential curve for tunneling. As shown in our previous study, the differential reaction energy and barrier height can be calculated accurately at a relatively low level of theory. Note it does not require any frequency calculation for the reactants or the transition state of the reaction R2.

B. Ratio of the reaction symmetry number, f_{σ}

$$f_{\sigma}=\frac{\sigma_2}{\sigma_1}. \tag{4}$$

Since the reaction symmetry numbers for reactions R1 and R2 are known, this factor is determined exactly.

C. Ratio of the partition function f_Q

$$f_Q(T)=\left(\frac{Q_2^{\ddagger}}{\Phi_2^R}\right)\Bigg/\left(\frac{Q_1^{\ddagger}}{\Phi_1^R}\right)=\left(\frac{Q_2^{\ddagger}}{Q_1^{\ddagger}}\right)\Bigg/\left(\frac{\Phi_2^R}{\Phi_1^R}\right). \tag{5}$$

Note that each partition function is a product of translational, rotational, and vibrational partition functions. It can be shown that the translational and rotational components yield a constant multiplicative factor in f_Q. The temperature dependent component of f_Q solely comes from the vibrational component. By rearranging the ratio of the partition functions of reactions R1 and R2 as shown in the second ratio of Eq. (5) above, an important point regarding reaction class can be made. To illustrate this point, we use a class of hydrogen abstraction reactions where the principal reaction of this class is the $H+CH_4$ reaction and different substituents R_1, R_2, and R_3, as shown in Fig. 1, yield different reactions in this class. The ratio of the vibrational partition functions at the transition states of the reactions R2 and R1 [the numerator of the second ratio in Eq. (5)] mainly comes from the substituents and the substituent effects on the frequencies of the reactive moiety. The same is true for the denominator, the ratio of the vibrational partition functions of the reactants of the reactions R2 and R1. The overall ratio further removes the principle components of the substituents. Thus, the ratio f_Q results mainly from the differences in the coupling or "cross" terms of the force constants of the two reactions at the transition states and reactants. If there is no coupling between the substituents and the reactive moiety then the vibrational component of f_Q is unity. In other words, the vibrational component of f_Q is the ratio of the differences in the effects of the substituents on vibrational frequencies of

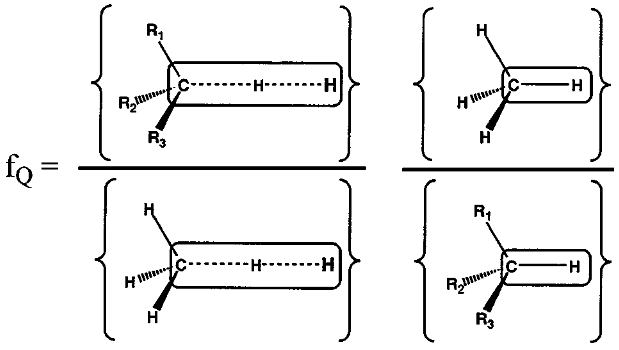

FIG. 1. Pictorial illustration of the factor of partition function f_Q. The reactive moiety consists of atoms in the box. Different substituents R_1, R_2, and R_3 yield different reactions in the class.

the reactive moiety and in the effects of the reactive moiety on the frequencies of the substituents at the transition state and at the reactants. Since these effects should have the same trends at the reactants and at the transition state, the temperature dependent component is significantly lessened in their ratio. Consequently, we expect that f_Q does not depend strongly on the temperature. As shown in Fig. 2, these ratios are nearly constant for a rather larger number of reactions in this class. Only a small temperature dependence in f_Q is observed for temperatures below 300 K for these reactions. For simplicity, we can make an approximation that f_Q is a constant and has the high temperature limit value of the $H+C_2H_6$ reaction. This would make only about 60% error in the rate coefficients for temperatures above 300 K for this reaction class. This is certainly an acceptable level of accuracy in kinetic modeling. Thus, f_Q can be predetermined for each class of reaction from frequency calculations for an additional small reaction in the class, so that vibrational frequency calculations for other reactions in the class are not required.

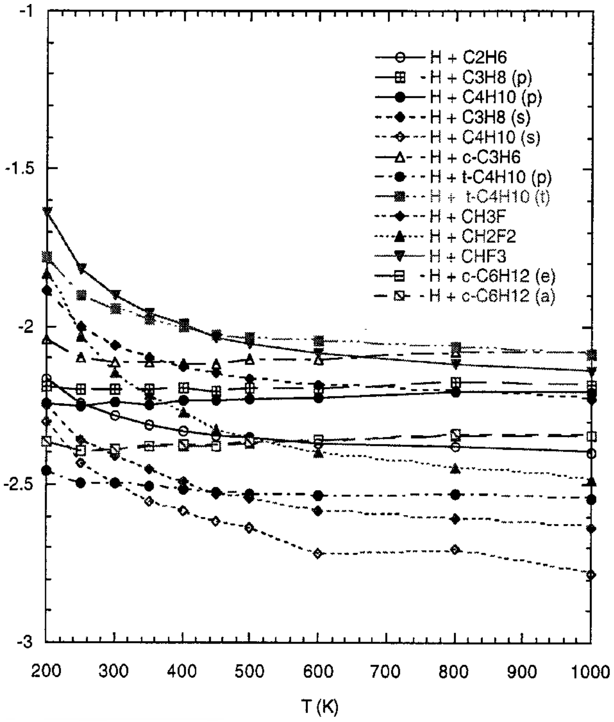

FIG. 2. Plot of $\ln f_Q$ vs T for a number of hydrogen abstraction reactions by the H atom. (p) denotes abstraction of primary hydrogen; (s) of secondary hydrogen; (t) of tertiary hydrogen; (e) of equatorial hydrogen; (a) of axial hydrogen.

D. Ratio of the potential energy, f_V

$$f_V=\exp\left\{-\frac{\Delta\Delta V^\ddagger}{k_BT}\right\}=\exp\left\{-\frac{(\Delta V_2^\ddagger-\Delta V_1^\ddagger)}{k_BT}\right\}, \tag{6}$$

where $\Delta\Delta V^\ddagger$, the difference in the classical barrier heights of reactions R2 and R1, respectively, can be rewritten as

$$\Delta\Delta V^\ddagger=\{E_2^\ddagger-E_1^\ddagger\}-\{E_2^R-E_1^R\}, \tag{7}$$

where E is the total potential energy. Thus, $\Delta\Delta V^\ddagger$ is the difference between the substituent effects in the potential energy at the transition state and at the reactants. From the expression in Eq. (7), interactions in the reactive moiety that are critical for accurate evaluation of the barrier height in the first term and reaction energy in the second term are removed by taking the difference from those of the principal reaction. As shown in previous studies,[26,27] $\Delta\Delta V^\ddagger$ can be accurately predicted from a relatively low level of theory.

In summary, the reaction class transition state theory requires the following information:

(1) Accurate potential energy information of the principal reaction, namely, structures, energies, and frequencies at least at the reactants, transition state, and products. Since the principal reaction is small, this condition can easily be met. Thermal rate constants for the principal reaction can be calculated from the above potential information using the TST method with Eckart tunneling corrections. However, they can also be calculated from a more accurate direct *ab initio* dynamics method, though this would require much more potential energy information along the reaction path. Note that experimental measurements can also be used.

(2) The ratio of the partition function, f_Q. As shown above, to a good approximation it can be assumed to be a conserved function of a given reaction class and can be determined from additional frequency calculations for another small reaction in the class.

Thermal rate constants for any other reactions in the class can be estimated from knowing only the differential reaction energy and barrier height. No frequency calculation, however, is required.

III. RESULTS AND DISCUSSION

We have chosen the class of hydrogen abstraction reactions by hydrogen atoms to test the RC-TST method. Particularly, several reactions were selected so as to provide severe tests of the theory and they are

$$H+CH_4\rightarrow H_2+CH_3, \tag{R1}$$

$$H+C_2H_6\rightarrow H_2+C_2H_5, \tag{R2}$$

$$H+H\text{-}CH_2CH_2CH_3\rightarrow H_2+CH_2CH_2CH_3, \tag{R3}$$

$$H + H\text{–}CH(CH_3)_2 \rightarrow H_2 + HC(CH_3)_2, \tag{R4}$$

$$H + C_3H_8 \rightarrow H_2 + \text{products}, \tag{R5}$$

$$H + c\text{-}C_3H_6 \rightarrow H_2 + c\text{-}C_3H_5, \tag{R6}$$

$$H + H\text{–}CH_2F \rightarrow H_2 + CH_2F, \tag{R7}$$

$$H + H\text{–}CHF_2 \rightarrow H_2 + CHF_2, \tag{R8}$$

$$H + H\text{–}CF_3 \rightarrow H_2 + CF_3. \tag{R9}$$

For this reaction class, R1 is the principal reaction. R2 is used to provide the f_Q factor. R3–R9 reactions are used to test the theory. For the principal reaction, accurate thermal rate calculations using canonical variational TST theory plus SCT tunneling correction were done previously;[7,8] we do not need to discuss further here. However, since the RC-TST method has its strength in its practicality, we envision that in actual applications of the theory, simple TST calculation and Eckart tunneling corrections for the principal reaction would be sufficient. The accuracy of the TST/Eckart method has been discussed in our previous studies.[9,25,28] In this case, geometries and frequencies of the reactants, transition state and products were calculated at the BH&HLYP/cc-pvdz level of theory. Single point energy calculations at the PMP4/cc-pvtz level were done to improve the accuracy of the calculated barrier height and reaction energy of the principal reaction. Our previous studies[8,29] have shown that the combination of BH&HLYP and PMP4 calculations provide sufficiently accurate potential energy information for thermal rate determination. For the R2 reaction, we only need to optimize the geometry and to calculate the frequencies of the stationary points at the BH&HLYP/cc-pvdz level. For R3–R9 reactions, only geometry optimizations of the stationary points were performed at the BH&HLYP/cc-pvdz level. Note that R3–R9 reactions were selected to provide different variations of reactions in this class that can severely test the new theory. In particular, reaction R3 is a primary hydrogen abstract reaction, whereas reaction R4 is a secondary abstract and R5 is the overall reaction. The ring constraint of cyclo-propane in R6 would severely test the reaction class concept in using potential energy information of the principal reaction H+CH$_4$. Electronegative fluorine substituents in R7–R9 reactions distort the geometry of transition states far from that of the principal reaction. In addition, these R3–R9 reactions provide a wide variation in the barrier height from 9.3 to 15.5 kcal/mol and in the reaction energy from −2.6 to 4.6 kcal/mol. The calculated differential barrier heights and reaction energies are listed in Table I. To calculate the barrier height or reaction energy for a particular reaction, the respective differential barrier height or reaction energy is added to that of the principal reaction. Note that the differential barrier heights and reaction energies calculated at the BH&HLYP compare well with the PMP4 results. Electronic structure calculations were done using the G98 program.[30]

TABLE I. Calculated differential reaction energies and barrier heights (kcal/mol).[a]

	$\Delta\Delta E = \Delta E - \Delta E(\text{R1})$		$\Delta\Delta V^{\ddagger} = \Delta V^{\ddagger} - \Delta V^{\ddagger}(\text{R1})$	
Reactions	PMP4	BHLYP	PMP4	BHLYP
H+H–CH$_3$(R1)	(2.90)[b]	(1.40)	(14.58)	(12.60)
H+H–CH$_2$CH$_3$	−3.01	−2.52	−2.83	−2.90
H+H–CH$_2$CH$_2$CH$_3$	−2.73	−2.27	−2.64	−2.57
H+H–CH(CH$_3$)$_2$	−5.45	−5.79	−5.26	−5.21
H+*c*-H–CHC$_2$H$_4$	4.51	4.38	0.22	0.13
H+H–C(CH$_3$)$_3$	−5.80	−8.47	−6.38	−7.11
H+H–CH$_2$F	−3.77	−3.11	−1.96	−2.31
H+H–CHF$_2$	−3.38	−3.04	−1.92	−2.32
H+H–CF$_3$	1.71	2.36	0.92	0.56

[a] PMP4 denotes PMP4/cc-pVTZ//BH&HLYP/cc-pVDZ; BHLYP denotes BH&HLYP/cc-pVDZ.

[b] Values in parentheses are the classical barrier height and reaction energy of the principal reaction.

A. H+C$_2$H$_6$

Arrhenius plot of the calculated rate constants for this reaction along with experimental data is shown in Fig. 3. Our calculated rate constants are in excellent agreement with experimental data[18,31–33] for a wide range of temperatures. Recall that no PMP4 single-point calculations were done for this reaction. The ratio of partition function, f_Q for this reaction class is determined from this and the principal reactions. f_Q is set equal to its high temperature limit of 0.095 and is used in estimating rate constants for reactions R3–R9.

B. H+C$_3$H$_8$

Arrhenius plots for the primary, secondary, and total hydrogen abstraction of C$_3$H$_8$ are shown in Figs. 4(a)–4(c),

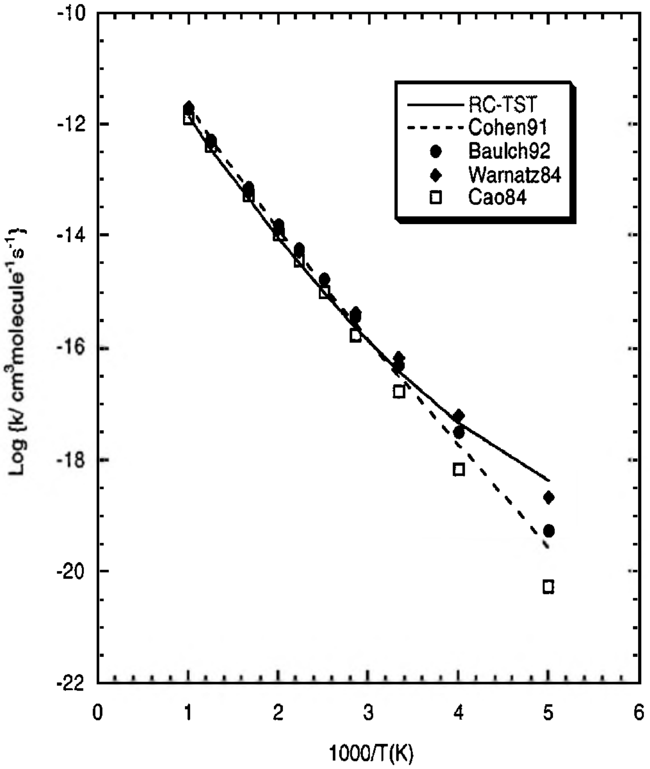

FIG. 3. Arrhenius plot of the H+C$_2$H$_6$→H$_2$+C$_2$H$_5$ reaction. Dashed line is from the TK-TST extrapolation of experimental data from Ref. 18. Filled circles are from Ref. 31; filled diamonds from Ref. 32; open squares from Ref. 33.

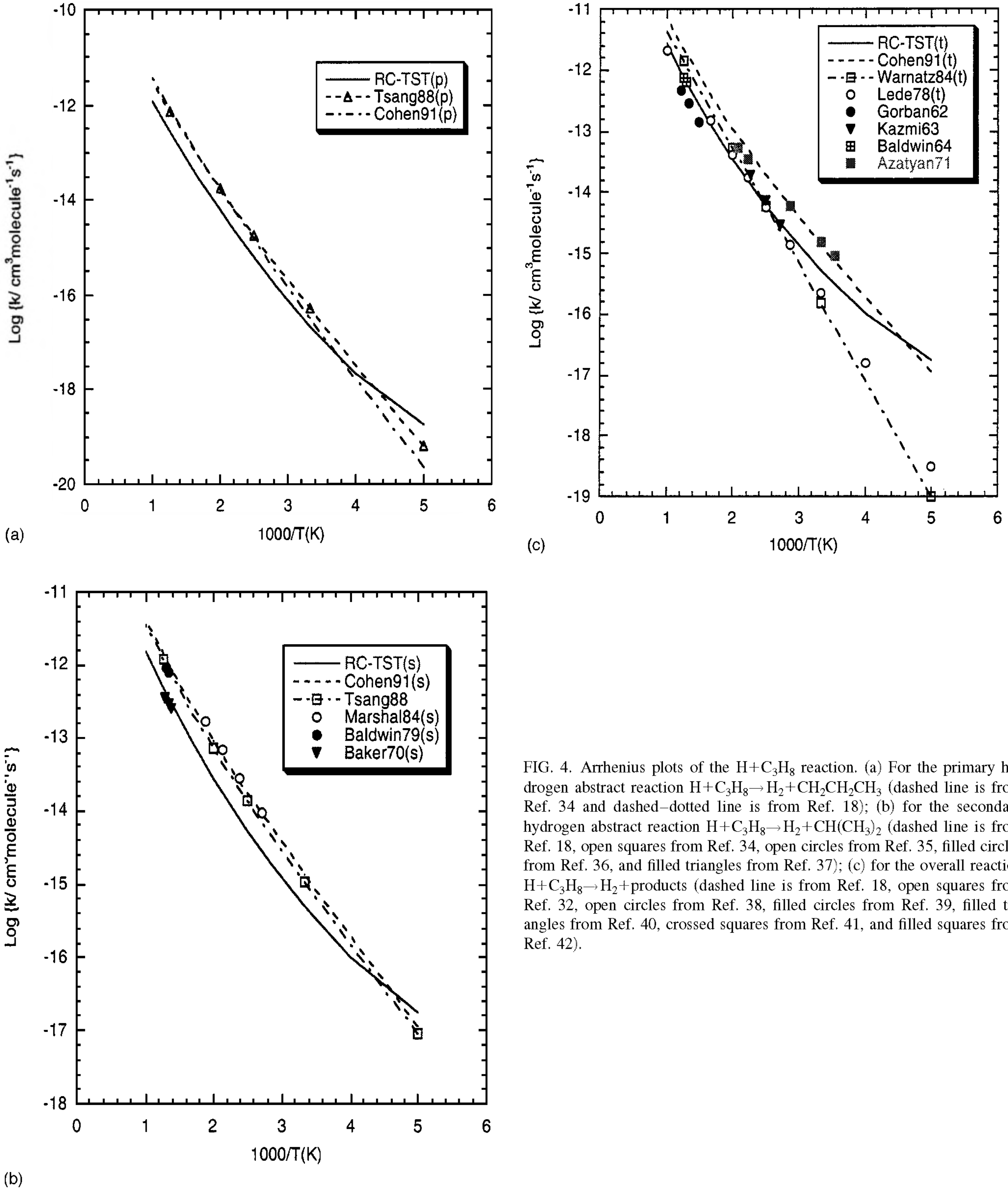

FIG. 4. Arrhenius plots of the $H+C_3H_8$ reaction. (a) For the primary hydrogen abstract reaction $H+C_3H_8 \rightarrow H_2+CH_2CH_2CH_3$ (dashed line is from Ref. 34 and dashed–dotted line is from Ref. 18); (b) for the secondary hydrogen abstract reaction $H+C_3H_8 \rightarrow H_2+CH(CH_3)_2$ (dashed line is from Ref. 18, open squares from Ref. 34, open circles from Ref. 35, filled circles from Ref. 36, and filled triangles from Ref. 37); (c) for the overall reaction $H+C_3H_8 \rightarrow H_2$+products (dashed line is from Ref. 18, open squares from Ref. 32, open circles from Ref. 38, filled circles from Ref. 39, filled triangles from Ref. 40, crossed squares from Ref. 41, and filled squares from Ref. 42).

respectively. Note that the experimental rate constants[18,34–37] for the primary and secondary hydrogen abstract are not from direct measurements but are derived either from fitting to a complex reaction mechanism or from the detailed balance condition. Thus, it is not informative to compare our calculated rate constants with the experimentally derived data. However, for the overall reaction where direct measurements can be done, our calculated overall rate constants shown in Fig. 4(c) are in excellent agreement with the available experimental data.[32,38–42]

C. H+*c*-C_3H_6

There were only two experimental studies[43,44] done by Marshall and co-workers for the hydrogen abstraction from

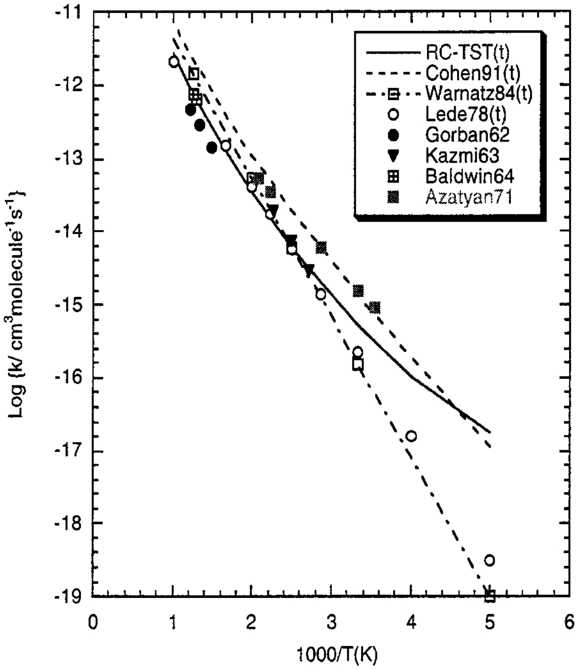

FIG. 5. Arrhenius plot for the H+ c-$C_3H_6 \rightarrow H_2 +$ c-C_3H_5 reaction. Dashed line is the TK-TST extrapolation of experimental data from Ref. 18, filled circles are experimental data from Ref. 44, and filled diamonds from Ref. 43.

cyclopropane. Our calculated results as shown in Fig. 5 agree much better with the earlier experiment,[43] whereas Cohen's TST interpolation results[18] fit better with the later one.[44] In any case, our calculated rate constants are within the experimental uncertainty.

D. H+CH_3F, H+CH_2F_2, H+CHF_3

Despite the fact that experimental data for these reactions are limited, our calculated rate constants for these reactions shown in Figs. 6–8, respectively, are in good agreement with the available experimental measurements.[25,45–47] Our results are slightly larger than those from accurate TST calculations by Berry *et al.*[48] though both are within the experimental uncertainty.

In summary, our calculated results for the R3–R9 reactions using the RC-TST method described above show excellent agreement with experimental data. This is very encouraging since limited electronic structure calculations, namely, only geometry optimizations of the stationary points at the BH&HLYP/cc-pvdz level of theory, were performed for these reactions. These results show that the RC-TST method can be a powerful tool for estimating kinetic parameters of a large number of elementary reactions in design of kinetic models for complex combustion systems, though more work needs to be done. Several issues have not been discussed in this study but are important to the development of this theory, namely (1) efficient methodology for obtaining the differential barrier height and reaction energy; (2) applications to other reaction classes such as those involving aromatic molecules; (3) treating reactions without barrier. These issues will be systematically addressed in future studies.

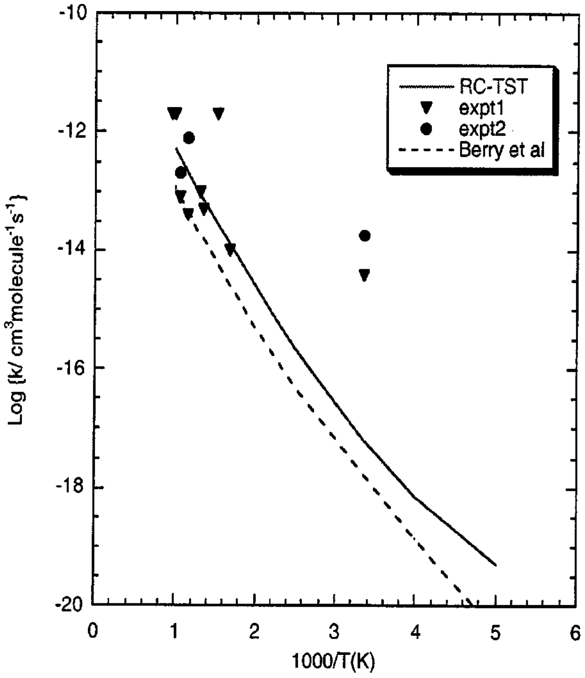

FIG. 6. Arrhenius plot for the H+$CH_3F \rightarrow H_2 + CH_2F$ reaction. Dashed line is the TST results from Ref. 48, filled triangles from Ref. 45, and filled circles from Ref. 46.

IV. CONCLUSION

We have presented a new formalism called Reaction Class Transition State Theory (RC-TST) for efficient calculations of thermal rate constants of reactions in a class from first principles. The RC-TST method is based on the transition state theory framework and properties of the reaction

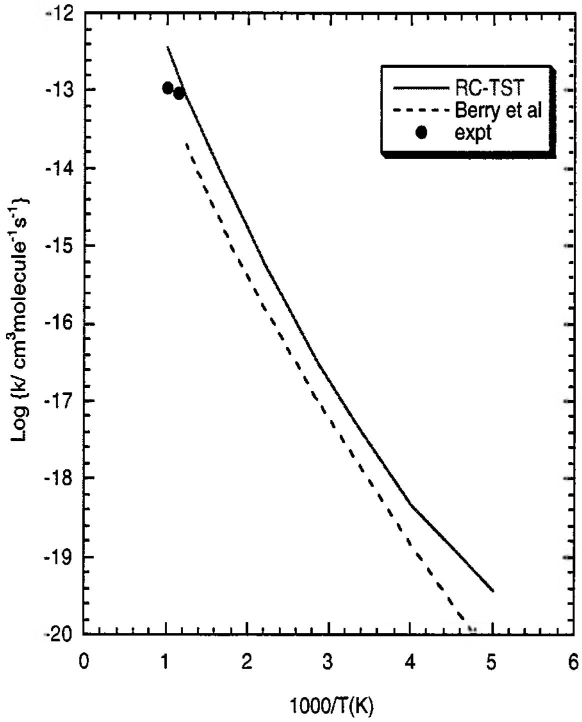

FIG. 7. Arrhenius plot for the H+$CH_2F_2 \rightarrow H_2 + CHF_2$ reaction. Dashed line is from Ref. 48 and filled circles from Ref. 45.

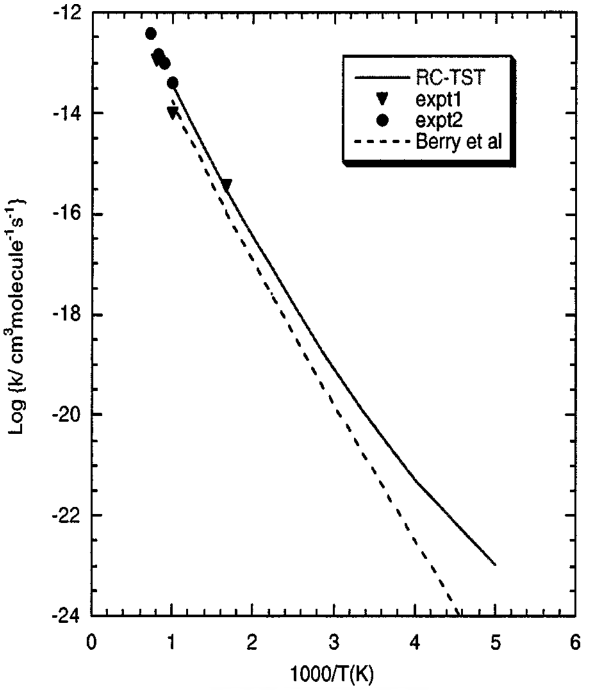

FIG. 8. Arrhenius plot for the $H+CHF_3 \rightarrow H_2+CF_3$ reaction. Dashed line is from Ref. 48, filled triangles from Ref. 45, and filled circles from Ref. 47.

class in deriving the expression for relative rate constants. With the readily available potential energy information for the principal reaction, thermal rate constants of any other reaction in the class can be efficiently estimated from only two energetic properties, namely, the differential barrier height and reaction energy. We have shown that these differential energetic properties can be calculated at a relatively low level of electronic structure theory and thus require much less computational demand than calculations of the actual barrier height and reaction energy. Consequently, the potential energy information required for the RC-TST method is much less than what is needed by the simple conventional TST method. We have applied the RC-TST method to several hydrogen abstraction reactions. The calculated rate constants are in excellent agreement with available experimental data in all test cases. This is particularly very encouraging since the practical implication of the RC-TST method in design of kinetic models for complex combustion systems is in fact enormous.

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