Kinetics of Hydrogen Abstraction Reactions from Polycyclic Aromatic Hydrocarbons by H Atoms

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An application of the Reaction Class Transition State Theory/Linear Energy Relationship (RC-TST/LER) is presented for the evaluation of the thermal rate constants of hydrogen abstraction reactions by H atoms from Polycyclic Aromatic Hydrocarbons (PAH). Two classes of reactions have been considered, namely hydrogen bonded to six- and five-membered rings, respectively, and twenty-two reactions have been used to develop the RC-TST/LER parameters. B3LYP and BH&HLYP density functional theory methods were used to calculate necessary potential energy surface information. Detailed analyses of RC-TST/LER reaction factors lead to the conclusion that rate constants for any reaction in these two classes can be approximated by those of its corresponding principal reaction corrected by the reaction symmetry factor. Specifically, for hydrogen abstraction from six-membered rings such as naphthalene and pyrene, $k(T) = (\sigma/\sigma_{H+C_6H_6})\, k_{H+C_6H_6} = (\sigma/6)\{1.42 \times 10^8 T^{1.77} \exp(-6570/T)\}(\text{cm}^3/\text{mol·s})$, and for hydrogen abstraction from five-membered rings such as acenaphthylene and acephenanthrylene, $k(T) = (\sigma/\sigma_{H+C_{12}H_8})\, k_{H+C_{12}H_8} = (\sigma/2)\{3.27 \times 10^8 T^{1.71} \exp(-8170/T)\}$ $(\text{cm}^3/\text{mol·s})$, where σ is the reaction symmetry number.

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAH) play an important role in the formation of combustion-generated particles such as soot, and their presence in atmospheric aerosols has been widely shown.[1] The formation of five-membered rings, detected in combustion effluent, is of great interest due to their genotoxic activity.[2] Acenaphthylene, for example, is suspected of being a major intermediate leading to soot formation, and existing kinetic models give poor predictions of its concentration in laminar flames. An essential requirement for reliable modeling of PAH growth is the availability of accurate kinetic parameters. Hence, an accurate analysis of the reaction rates is required to avoid even relatively small uncertainties on kinetic data. Such uncertainties may induce substantial deviations in the model predictions of PAH concentrations or soot yields due to accumulation of errors in the large number of subsequent growth steps necessary for the description of the formation of larger compounds.[3]

For many combustion systems, kinetic models often consist of thousands of elementary reactions, and it is therefore impractical to carry out calculations of the thermal rates for every single reaction. Among the existing methods, the Transition State Theory[4] (TST) is the simplest and most cost-effective, and it requires only geometries, energies, and vibrational frequencies of the reactants and transition states. However, the large size of PAH molecules limits the use of accurate quantum chemistry methods for obtaining such information. Since experimental kinetic data for reactions involving PAH species are generally not available, especially over an extended range,

one is forced to estimate rate coefficients.[5] A common practice is to approximate the unknown kinetic parameters by those for similar reactions. A better approach is to employ the Evan-Polanyi linear free-energy[6,7] 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 uncertainties in the estimated constants. In the case where some limited rate information is available, it is possible to use a procedure called the Thermochemical Kinetics TST (TK-TST) method developed by Benson and co-workers[8] and later defined by Cohen and co-workers[9,10] to extrapolate to other temperatures.

Recently, Truong and co-workers[11] have introduced the concept of reaction class into both electronic structure and dynamical calculations. This method recognizes that reactions in a given class have the same reactive moiety, and their potential energy surfaces along the reaction coordinate are very similar. The Reaction Class Transition State Theory (RC-TST) theory provides a rigorous methodology for estimating thermal rate constants of any reaction in a class from the smallest reaction, i.e., the principal reaction in the class, using the relative classical barrier and reaction energy. Furthermore within the RC-TST framework, it is possible to establish a Linear Energy Relationship (LER) between the classical barrier and the reaction energy. Therefore, to a high degree of accuracy, it is possible to predict rate constants of any reaction in the class by knowing its reaction energy only. This combined RC-TST/LER approach was used successfully in predicting rate constants for a large number of hydrogen abstraction reactions in the H + H−C(sp^3) class.

In this study, we apply the RC-TST/LER method to study hydrogen abstraction by H atom from different PAH. In particular, two classes of PAH were considered; one consists

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Benzene (C$_6$H$_6$)
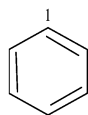
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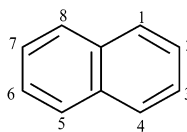
Anthracene (C$_{14}$H$_{10}$)
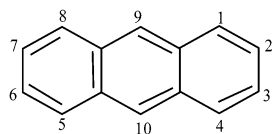
Phenanthrene (C$_{14}$H$_{10}$)
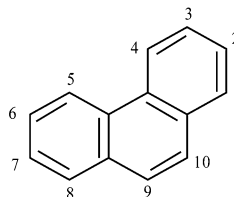
Pyrene (C$_{16}$H$_{10}$)
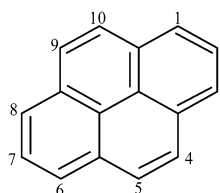
Acenaphthylene (C$_{12}$H$_8$)
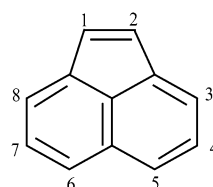
Acephenanthrylene (C$_{16}$H$_{10}$)
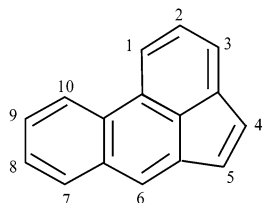
Aceanthrylene (C$_{16}$H$_{10}$)
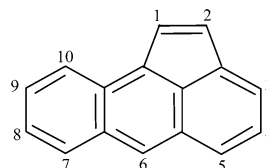
Cyclopenta[cd]pyrene (C$_{18}$H$_{10}$)
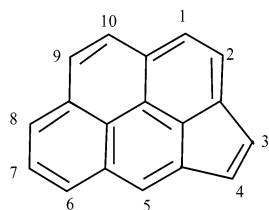
Dicyclopenta[cd,jk]pyrene (C$_{20}$H$_{10}$)
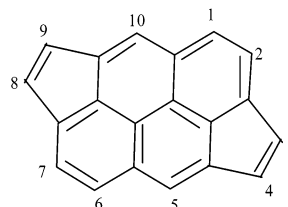
Cyclopenta[fg]benzo[ghi]perylene C$_{24}$H$_{12}$)
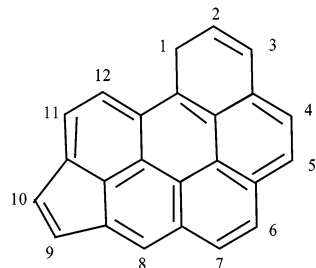
Figure 1. List of Polycyclic Aromatic Hydrocarbons.

of only six-membered ring compounds such as benzene and naphthalene and the other has five-membered rings such as acenaphthylene and aceanthrylene. Twenty-two reactions total were used to derive the reaction class parameters. It is important to point out that such parameters need to be determined only

once for each reaction class. Subsequently, with these parameters, rate constants for any other reaction in these two classes can be predicted from their reaction energies only. The compounds considered for this study are reported in Figure 1 with their IUPAC nomenclature.

2. Methodology

The Reaction Class Transition State Theory is based on the transition state theory framework within the reaction class approach in deriving the expression for relative rate constants. With the available potential energy information for the principal reaction, i.e., the smallest reaction in a given class, thermal rate constants of any other reaction in the class can be estimated from the differential barrier height and reaction energy.

The rate constant of an arbitrary reaction ($k_a(T)$) in a given reaction class is proportional to the rate constant of the principal reaction ($k_p(T)$) by a temperature-dependent function $f(T)$:

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

$f(T)$ can be factored into four different components:

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

where f_κ, f_σ, f_Q, and f_V are the tunneling, symmetry, partition function, and potential energy factors, respectively. The symmetry factor is known from structures, whereas other factors must be determined once for each reaction class. These factors can be efficiently evaluated from a subset of reactions in the class by using the reaction class approach as described in details elsewhere.[11] Furthermore, within the reaction class transition state theory, it is possible to establish a linear relationship between the classical barrier and the reaction energy so that only the reaction energy is required to predict the thermal rate constants for any reaction in the class.

To summarize, to apply the reaction class transition state theory to predict rate constants for any reaction in a given class, we first need to establish the following information:

1. Accurate thermal rate constants of the principal reaction (k_p). Such information can be calculated from first principles or taken from experiments.

2. Determining f_Q and f_κ from a small subset of reactions in the class. These factors can be represented by some temperature-dependent expressions.

3. LER to estimate the barrier height from the corresponding reaction energy. This information is used to calculate the f_V factor. This LER can be established from calculated barrier heights and reaction energies for a small subset of reactions in the class.

We discuss below in detail how such information is determined.

2.1. Electronic Structure Calculations. The list of the reactions considered in this study is reported in Table 1.

Geometries and frequencies of the reactants, transition states, and products were calculated by using the hybrid density functional B3LYP method (i.e., Becke's three-parameter non-local exchange functional[12] with the nonlocal correlation function of Lee, Yang, and Parr[13,14]), with the 6-31G (d,p) basis set. The B3LYP method is known to give rather accurate reaction energies, geometries, and vibrational frequencies. Such information is required for determining thermodynamic properties of stable species. However, B3LYP underestimates the activation energies. Limiting by the size of the molecular species considered in this study, to obtain more reliable barrier heights, we have carried out single-point calculations at the BH&HLYP/6-31G(d,p) level of theory. The BH&HLYP method predicts rather accurate barrier heights, particularly for hydrogen abstraction reactions by a radical such as those in this study in comparisons with more accurate calculations.[15] Normal-mode analyses were carried out to verify the nature of the stationary points by the number of imaginary frequencies (NIMF), i.e.,

TABLE 1: List of Reaction Classes

	Class 1
R1	$C_6H_6 + H = C_6H_5 + H_2$
R2	$C_{10}H_8 + H = 1*C_{10}H_7 + H_2$
R3	$C_{10}H_8 + H = 2*C_{10}H_7 + H_2$
R4	$phen + H = 1*phen + H_2$
R5	$phen + H = 9*phen + H_2$
R6	$anth + H = 1*anth + H_2$
R7	$anth + H = 2*anth + H_2$
R8	$anth + H = 10*anth + H_2$
R9	$C_{16}H_{10} + H = C_{16}H_9 + H_2$
R10	$C_{12}H_8 + H = 3*C_{12}H_7 + H_2$
R11	$C_{12}H_8 + H = 5*C_{12}H_7 + H_2$
R12	$acephe + H = 7*acephe + H_2$
R13	$aceanth + H = 9*aceanth + H_2$
R14	$C_{18}H_{10} + H = 6*C_{18}H_9 + H_2$
R15	$C_{24}H_{12} + H = 3*C_{24}H_{11} + H_2$
R16	$C_{20}H_{10} + H = 2*C_{20}H_9 + H_2$
	Class 2
R17	$C_{12}H_8 + H = 1*C_{12}H_7 + H_2$
R18	$acephe + H = 5*acephe + H_2$
R19	$aceanth + H = 2*aceanth + H_2$
R20	$C_{18}H_{10} + H = 4*C_{18}H_9 + H_2$
R21	$C_{24}H_{12} + H = 9*C_{24}H_{11} + H_2$
R22	$C_{20}H_{10} + H = 4*C_{20}H_9 + H_2$

NIMF = 0 for a stable species and NIMF = 1 for a transition state. Animation of the normal mode corresponding to the imaginary frequency was done for each reaction to confirm the right transition state. All calculations were performed using the Gaussian 98 program.[16]

3. Results and Discussion

3.1. Principal Reactions. As mentioned earlier, we first need to determine accurate thermal rate constants for the principal reactions of the two classes, which, in particular, are abstractions of H bonded to six-membered rings (Class 1) and to five-membered rings (Class 2) by H atoms (see Table 1). These classes contain acenes, e.g., phenes and pery-condensed poly-arenes. Aromatic hydrocarbons with external cyclopentafused five-membered rings (CP–PAH) belong to the class of non-alternant polycyclic aromatic hydrocarbons.[17]

The principal reactions for H abstraction from six-membered rings and five-membered rings, respectively, are

$$C_6H_6 + H = C_6H_5 + H_2 \tag{R1}$$

and

$$C_{12}H_8 + H = 1*C_{12}H_7 + H_2. \tag{R17}$$
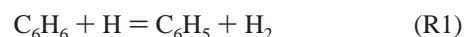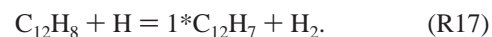
Most of the kinetic schemes present in the literature that describe the H abstraction from PAH use the value obtained in a shock-tube study by Kiefer et al.[18] for the reaction of H with benzene to produce phenyl and hydrogen.[19–22] Recently, Mebel et al.[23] determined thermal rate constants using the transition state theory plus tunneling corrections for the $C_6H_5 + H_2 = C_6H_6 + H$ reaction where the potential energy surface information was calculated at a rather accurate G2M (rcc,MP2) level of theory. This calculated rate constant showed excellent agreement with available experimental data. G2M predicts the reaction energy of 11.1 kcal/mol as compared to the value of 8.7 ± 0.6 kcal/mol based on the experimental bond energies of the C–H bond of benzene and the H–H bond of H_2. Thus, to obtain the rate constant for the H + C_6H_6 reaction, the authors combined rate constants for the $H_2 + C_6H_5$ reaction with the calculated equilibrium constants based on G2M molecular

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TABLE 2: Calculated Classical Barriers (kcal/mol) for the Principal Reactions $C_6H_6 + H = C_6H_5 + H_2$ and $C_{12}H_8 + H = 1*C_{12}H_7 = H_2$

level of theory	$C_6H_6 + H$	$C_{12}H_8 + H$
B3LYP/6-31G(d,p)	11.13[b]	14.07[b]
BH&HLYP//B3LYP	15.07[b]	17.73[b]
G2M(rcc,MP2)	19.90[a]	
Corrected G2M	17.5[a]	

[a] Taken from ref 23. Corrected G2M value is determined from the G2M barrier of the reverse reaction and experimental value of the reaction energy. [b] Present study.

parameters and the experimental heat of reaction at 0 K. In this case, the effective classical barrier height for the H + C_6H_6 reaction is 17.5 kcal/mol as compared to the G2M value of 19.9 kcal/mol. It is interesting to point out that the Mebel et al. study provides useful information to validate the accuracy of the DFT theory used in this study. The barrier heights for the R1 and R17 reactions calculated at different levels of theory are listed in Table 2.

Our results confirm a previous finding that B3LYP greatly underestimates the barrier for hydrogen abstraction reactions by radicals while BH&HLYP performs much better in this regard. Although the BH&HLYP barrier is 2.4 kcal/mol below the corrected G2M value, as discussed below our calculated rate constant for reaction R1 is in excellent agreement with values obtained in a shock-tube study by Kiefer et al.[18]

For H abstraction from five-membered ring systems such as acenaphthylene (R17), there has not been any experimental data available. For this reason, the rate expression for the R1 reaction has been used for such reactions in previous combustion modeling. The validity of such an approximation has not been discussed, though one can expect that the reactivity of five-membered ring systems would be very different from those of six-membered ring systems. From Table 2, the BH&HLYP barrier height for this reaction is 17.7 kcal/mol, which is 2.6 kcal/mol higher than that of the R1 reaction. Thus, assuming that R17 has the same rate constants as of R1 would overestimate the rate constant for R17 by a factor of 78 at room temperature. We have calculated thermal rate constants for both R1 and R17 reactions using the conventional Transition State Theory augmented with one-dimensional Eckart tunneling corrections. B3LYP structural and vibrational information with BH&HLYP corrected barrier were used. These calculations were done using our web-based Vklab tool.[24] Figure 2 shows the comparison between the calculated rate constants for the R1 and R17 reactions along with experimental data, which are only available for the R1 reaction.

Notice that our calculated rate constant for R1 agree very well with experimental data from Kiefer et al.[18] The Mebel et al. results[23] are smaller at low temperatures while other indirect data[25,26] are noticeably larger. Due to the higher barrier, the rate constants for R17 are much lower than those of R1, particularly in the low-temperature range. In summary, the computed Arrhenius expressions for thermal rate constants derived in this work for R1 and R17, respectively, are

$$k_{R1} = 1.42E8 \ T^{1.77} \exp(-6570/T)) \ \text{cm}^3/\text{mol·s} \quad (3)$$

and

$$k_{R17} = 3.27E8 \ T^{1.71} \exp(-8170/T) \ \text{cm}^3/\text{mol·s} \quad (4)$$

3.2. Linear Energy Relationships. Figure 3 shows the Linear Energy Relationship (LER) between the B3LYP reaction
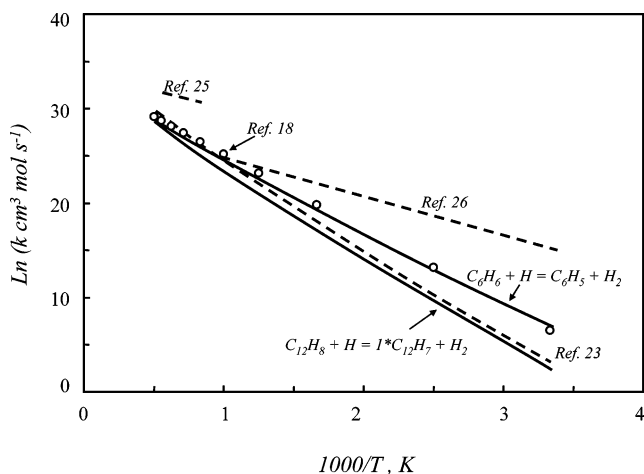

Figure 2. Computed reaction rates for $C_6H_6 + H = C_6H_5 + H_2$ and $C_{12}H_8 + H = 1*C_{12}H_7 + H_2$ (solid lines), together with data present in the literature (refs 18, 23, 25, 26).
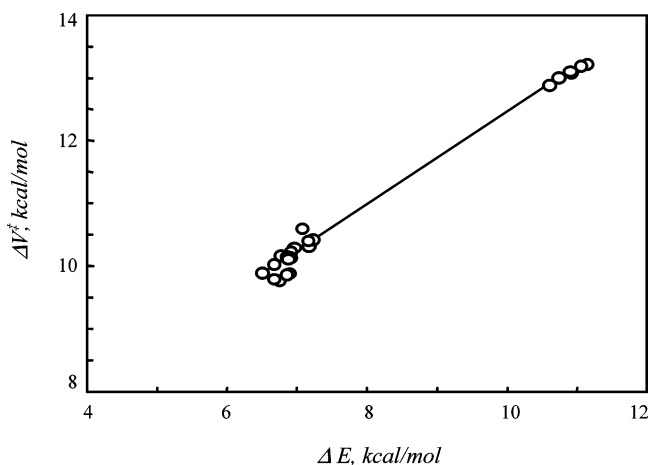

Figure 3. Linear energy relationship between reaction energy ΔE computed at B3LYP/6-31G(d,p) level and reaction barrier heights ΔV calculated at BH&HLYP/6-31G(d,p) level of theory for the reactions listed in Table 1.

energies and BH&HLYP barrier heights for H abstraction by H atom for the reactions listed in Table 1.

It was possible to fit the results for the two reaction classes considered with a single LER equation, namely:

$$\Delta V^{\neq} = 0.74 \ \Delta E + 5.06 \ \text{kcal/mol} \quad (5)$$

The potential energy factor, f_V, is defined as

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

where $\Delta V_a^{\neq} - \Delta V_p^{\neq}$ is the difference in the barrier heights of the target and principal reactions, respectively. The calculated reaction energies and the reaction barrier heights for all the compounds analyzed are listed in Table 3, together with the deviations between calculated barrier heights from the linear energy relationships (LER) (eq 5) and those from full quantum calculations.

The average deviations of reaction barrier heights predicted by B3LYP reaction energies using eq (5) for the six-membered and CP-PAH classes are 0.0008 and 0.001

TABLE 3: Reaction Barriers ($\Delta V^{\neq}$), Reaction Energies (ΔE), and Deviations between Calculated Barriers and LRE Barriers (units: kcal/mol)

reaction	ΔE^a	$\Delta V^{\neq b}$	$\Delta V^{\neq c}_{LER}$	$|\Delta V^{\neq} - \Delta V^{\neq}_{LER}|$
R1	6.72	15.07	15.19	0.12
R2	6.88	15.34	15.29	0.054
R3	6.86	15.19	15.28	0.084
R4	6.88	15.38	15.29	0.087
R5	6.83	15.34	15.25	0.089
R6	6.85	15.23	15.27	0.038
R7	6.82	15.08	15.25	0.16
R8	7.04	15.49	15.39	0.096
R9	7.20	15.53	15.49	0.046
R10	6.48	15.15	15.04	0.10
R11	7.15	15.31	15.45	0.14
R12	6.75	15.33	15.20	0.12
R13	6.65	15.02	15.14	0.12
R14	6.94	15.39	15.32	0.070
R15	7.14	15.45	15.45	0.0087
R16	6.65	15.12	15.14	0.022
R17	10.88	17.73	17.77	0.033
R18	10.71	17.69	17.66	0.034
R19	11.12	17.84	17.91	0.074
R20	11.03	17.84	17.85	0.012
R21	10.87	17.84	17.76	0.086
R22	10.57	17.58	17.57	0.0053

[a] Calculated at B3LYP/6-31G (d,p) level of theory. [b] Calculated at BH&HLYP//B3LYP level of theory. [c] ΔV_{LER} was calculated from the LER expression by substituting B3LYP/6-31G(d,p) reaction energies into eq (5).

TABLE 4: Calculated Symmetry and Tunneling Factors

reaction	f_σ	f_κ^a ($T = 300$ K)	f_κ^b ($T = 300$ K)
R1	$(6)^c$	$(2.67)^c$	$(2.67)^c$
R2	1.33	0.99	0.95
R3	1.33	0.99	0.99
R4	1.66	0.98	1.00
R5	1.66	1.00	1.00
R6	1.66	0.99	1.00
R7	1.66	0.99	0.99
R8	1.66	0.98	1.00
R9	1.66	0.97	0.99
R10	1	1.07	1.00
R11	1	0.99	0.99
R12	1.33	1.00	1.00
R13	1.33	1.02	1.00
R14	1.33	0.95	1.00
R15	1.66	0.99	0.99
R16	1	1.02	0.95
R17	$(2)^c$	$(2.04)^c$	$(2.04)^c$
R18	1	1.01	1.00
R19	1	0.98	0.99
R20	1	0.99	0.99
R21	1	1.00	1.00
R22	2	1.02	1.00

[a] Calculated using imaginary frequency, forward and reverse barriers obtained through BHandLYP/6-31G (d,p) level of theory. [b] Calculated using the RC-TST theory. [c] Values in parentheses are symmetry number and tunneling coefficients of the principal reactions.

kcal/mol, respectively. The absolute deviations of reaction barrier heights between LERs and full quantum calculations are smaller than 1 kcal/mol for all reactions, hence smaller than the systematic errors of the computed reaction barriers from full quantum calculations. Thus, eq (5) is expected to give a good estimation of reaction barrier heights for the reactions analyzed.

3.3. Symmetry Number Factor. The symmetry number factor, f_σ, is defined as the ratio of symmetry numbers of the target reaction and principal reaction,

$$f_\sigma = \frac{\sigma_a}{\sigma_p} \quad (7)$$

Values of f_σ for the considered reactions are listed in Table 4. The symmetry numbers for R1 and R17 are 6 and 2, respectively.

For any reaction in either class, this factor can be determined from the topology of the reactant.

3.4. Tunneling Factor. The tunneling factor f_κ

$$f_\kappa = \frac{\kappa_a(T)}{\kappa_p(T)} \quad (8)$$

is the ratio of tunneling coefficients of the target and the principal reaction, respectively. We use the unsymmetrical Eckart potential[27] to calculate the tunneling coefficients, which requires only the imaginary frequency and forward and reverse barrier heights of a given reaction. Furthermore, the RC-TST method assumes 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. The imaginary frequencies used for the calculation of f_κ for the six- and five-membered classes are $905i$ and $756i$ cm^{-1}, respectively. Thus, only the differential barrier information $\Delta\Delta V^{\neq}$ (eq 6) is needed to calculate the tunneling correction for any reaction in the class. Table 4 reports the calculated tunneling factors for

the reactions listed in Table 1 using barrier heights calculated by the BH&LYP/6-31G(d,p) level of theory (exact) and the ones obtained through the LER relationship (eq 6) with RC-TST approximations. Notice that the approximated tunneling factors agree very well with the exact values, indicating that the reaction class approximations mentioned above are valid. These factors for the reactions considered in both classes are close to unity for temperatures above 300 K. In Table 4, we listed these values only at 300 K, but since tunneling is more important at low temperatures, deviations would be largest at the lower temperature limit. These results indicate that the tunneling corrections for all reactions in each class are similar to those of the corresponding principal reaction. Consequently, for simplicity, we approximate these factors to be unity for both classes.

3.5. Calculation of Partition Function Factor. The ratio of the partition function, f_Q, is represented by

$$f_Q(T) = \left(\frac{Q_a^{\neq}(T)}{\Phi_a^R(T)}\right) \Big/ \left(\frac{Q_p^{\neq}(T)}{\Phi_p^R(T)}\right) \quad (9)$$

where $Q^{\neq}$ and Φ^R are the partition functions of the transition states and reactants of the target and principal reactions. Each partition function is the product of translational, rotational, and vibrational factors. It can be shown that the translational and rotational components yield a constant multiplicative factor in f_Q. 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 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 for the reactants and for the transition states of all reactions in a
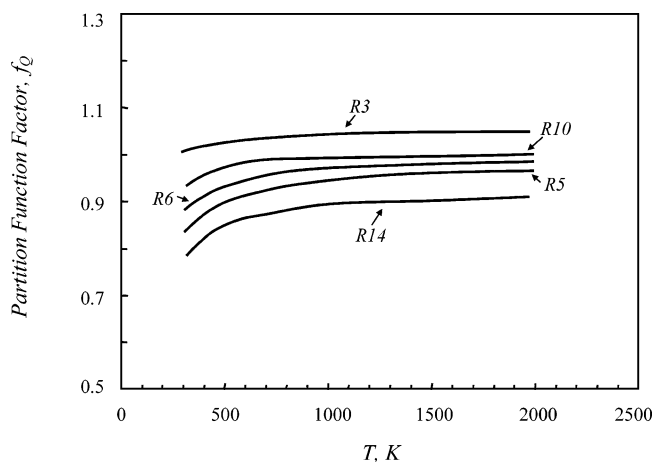
Hydrogen Abstraction from PAH by H Atoms

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Figure 4. Partition function factors f_Q versus temperature for some reactions listed in Table 1.

TABLE 5: RC-TST/LER Derived Parameters

$$k_p(T) = k_p(T) f_\kappa f_\sigma f_V f_Q$$
$$f_V(T) = \exp[-(\Delta\Delta V^{\neq})/k_B T]$$

$k_p(T)$	Class 1 [cm³/mol·s]	$1.42E8\ T^{1.77}\exp(-6570/T)$
$k_p(T)$	Class 2 [cm³/mol·s]	$3.27E8\ T^{1.71}\exp(-8170/T)$
$\Delta V^{\ddagger}$	[kcal/mol]	$0.74\ \Delta E + 5.06$
f_σ		see Table 4 for examples
$f_\kappa(T)$	Class 1	$1.01\ T^{-1.26E-3}\exp(-2.351/T)$
$f_\kappa(T)$	Class 2	$1.02\ T^{(-7.41E-3)}\exp(1.45/T)$
$f_Q(T)$	Class 1	$1.13\ T^{-0.0166}\exp(-55.58/T)$
$f_Q(T)$	Class 2	$9.88E-1\ T^{1.48E-3}\exp(2.19/T)$

given class, the temperature-dependent component is significantly lessened in their ratio. Consequently, we expect that f_Q should not depend strongly on temperature. Figure 4 shows the temperature dependence of f_Q for some of the reactions reported in Table 1. The ratios are nearly constant for a rather large number of reactions in these classes. Only small temperature dependences are observed for the values of f_Q at temperatures below 500 K.

For simplicity, f_Q as a function of the temperature for the H-abstraction from six-membered rings (Class 1) was fitted by the general expression:

$$f_Q = 1.13T^{-0.0166}\exp(-55.58/T) \tag{10}$$

and for H-abstraction from CP−PAH (Class 2) the expression is

$$f_Q = 9.88E-1\ T^{1.48E-3}\exp(2.19/T) \tag{11}$$

For Class 2, f_Q is essentially 1 over the temperature range studied, 300−2000 K. In fact, both factors are close to unity and thus for simplicity can also be approximated to be one.

3.6. RC-TST/LER Rate Constants. For any given reaction in the two classes, the rate constant ($k^{RC-TST/LER}$) can be computed from eqs (1) and (2). Table 5 summarizes the expressions for the parameters needed to calculate $k^{RC-TST/LER}$.

Since experimental data are not available for H-abstraction reactions from PAH larger than benzene, we have therefore evaluated the accuracy of the methodology by comparing the reaction rates computed using the TST/Eckart method with the ones obtained using the RC-TST/LER. Figures 5a and 5b show the Arrhenius plots for reactions
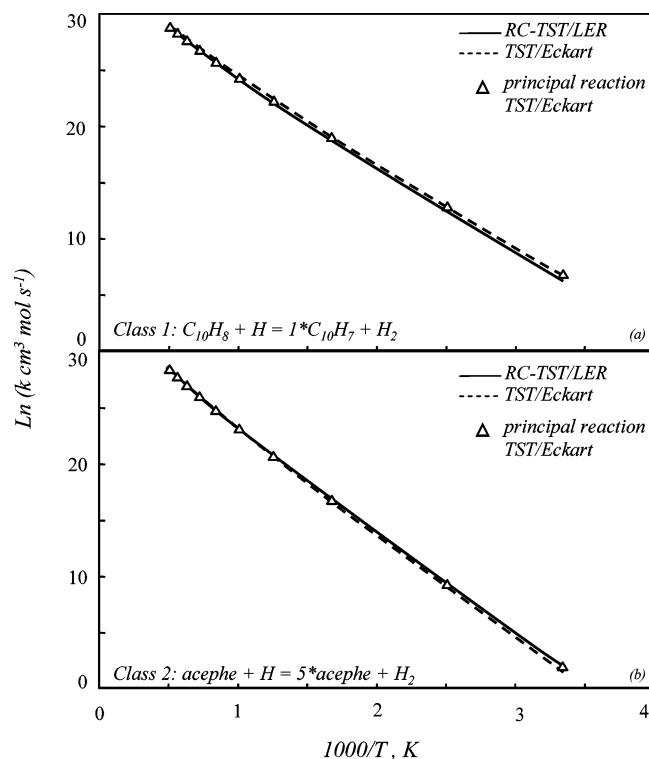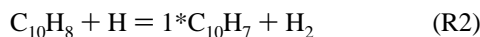
$$C_{10}H_8 + H = 1*C_{10}H_7 + H_2 \tag{R2}$$

Figure 5. Arrhenius plots obtained using TST/Eckart and RC-TST theories for reactions $C_{10}H_8 + H = 1*C_{10}H_7 + H_2$ Class 1(a) and reaction acephe + H = 5* acephe + H_2 Class 2 (b). The points represents the values computed for the principal reactions for the two classes.

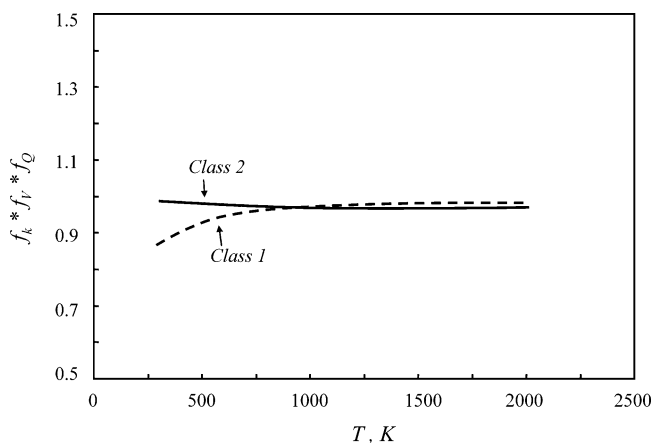**Figure 6.** Relative rate factor $f'(T) = f_Q f_\kappa f_V$ for for Class 1 and Class 2.

and

$$acephe + H = 5*acephe + H_2 \tag{R18}$$

We also plotted in Figure 5 rate constants of the corresponding principal reactions.

The predicted total rate constants obtained through the RC-TST/LER method are in excellent agreement with the ones calculated using explicitly the TST/Eckart method. It is also interesting to note that rate constants for these two reactions are quite close to those of their corresponding principal reactions. This leads us to take the analysis one step further by plotting the relative rate factors, $f'(T)$, as a product of $f_Q f_\kappa f_V$ for both reaction classes in Figure 6.

The relative rate factors $f'(T)$ for both reaction classes are close to unity for the temperature range from 300 to 2000 K

with about 10% deviation at lower temperatures for the abstraction of six-membered ring class. As a consequence, the rate constants for any reactions in these two classes can be approximated by those of their corresponding principal reactions corrected by the symmetry reaction factor, i.e., $k_a(T) = f_\sigma k_p(T)$, thus no extra calculation is needed.

4. Conclusion

We have applied the Reaction Class Transition State Theory with the Linear Energy Relationship for prediction of thermal rate constants of hydrogen abstraction reactions by hydrogen atom in two classes of compounds, viz., six-membered PAH, e.g., benzene, naphthalene, and five-membered PAH, e.g., acenaphthylene, aceanthrylene. Twenty-two reactions were studied. Potential energy surfaces for these reactions were calculated at the B3LYP and BH&HLYP levels of theory using the 6-31G(d,p) basis set. Thermal rate constants for the principal reactions, i.e., $H + C_6H_6 = H_2 + C_6H_5$ for abstraction from six-membered rings and $H + C_{12}H_8 = H_2 + 1^*C_{12}H_7$ for abstraction from five-membered rings, were calculated using the transition state theory augmented by the one-dimensional Eckart tunneling corrections. Our calculated rate constants for the $H + C_6H_6$ reaction are in excellent agreement with available experimental data. Using information from the twenty-two reactions considered, we have developed RC-TST/LER parameters for predicting rate constants of any reaction in these two classes from only its reaction energy. Interestingly, our detailed analysis of these parameters has led to an important conclusion. Specifically, rate constants for any reaction in these two classes can be approximated by those of its corresponding principal reaction corrected by the reaction symmetry factor. Consequently, no additional calculation is needed.

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