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Thermochemical Kinetic Analysis of Tunneling and the Incorporation of Tunneling Contributions in Thermochemical Kinetics

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Abstract: We partition the phenomenological enthalpy and entropy of activation for five hydrogen atom transfer reactions, $H + H_2 \rightarrow H_2 + H$, $D + H_2 \rightarrow HD + H$, $H + D_2 \rightarrow HD + D$, $O(^3P) + H_2 \rightarrow OH + H$, and $OH + H_2 \rightarrow H_2O + H$ into substantial and nonsubstantial contributions. The latter, which are not considered explicitly in previous thermochemical kinetic models, are very significant. The present analysis could serve as the start of a semiempirical data base for the inclusion of variational and tunneling effects in future thermochemical kinetic models.

1. Introduction

From a knowledge of the structure and vibrational frequencies of bound chemical species, statistical mechanics provides the prescription for the direct calculation of thermochemical data such as heats of formation of stable compounds and heat release and equilibrium constants for chemical reactions.[1] The structural and energetic information can be reduced into thermodynamic quantities, the enthalpy and entropy, which can be accurately approximated with bond additivity and group additivity relationships. The quasi-thermodynamic formulation of conventional transition-state theory[2,3] allows these ideas to be extended to the estimation of reaction rate constants.

In thermochemical kinetics a quasi-equilibrium is postulated between reactants and a transition-state complex, and the conventional transition-state theory rate constant $k^\ddagger(T)$ is expressed in terms of the associated unitless quasi-equilibrium constant $K_p^\ddagger(T)$ as

$$k^\ddagger(T) = \frac{k_B T}{h}(C^\circ)^{\Delta n^\ddagger} K_p^\ddagger(T) \tag{1}$$

In eq 1, k_B is Boltzmann's constant, T is the temperature, h is Planck's constant, C° is the concentration in the standard state, and $\Delta n^\ddagger$ is the stoichiometric change in the number of moles in passing from the reactants to the transition state. The equilibrium constant can be expressed in terms similar to the usual thermodynamic quantities

$$K_p^\ddagger(T) = \exp(-\Delta_\ddagger G_T^\circ / RT) \tag{2}$$

where $\Delta_\ddagger G_T^\circ$ is the conventional transition-state theory approximation to the standard-state free energy of activation at temperature T and R is the gas constant. (The standard state for all equations and tables in this paper is the ideal gas state at 1 atm.) The free energy of activation can be further factored

$$\Delta_\ddagger G_T^\circ = -T\Delta_\ddagger S_T^\circ + \Delta_\ddagger H_T^\circ \tag{3}$$

where $\Delta_\ddagger H_T^\circ$ and $\Delta_\ddagger S_T^\circ$ are the enthalpy and entropy of activation, respectively, at temperature T and are related to the equilibrium constant by the standard thermodynamic relationship

$$\Delta_\ddagger H_T^\circ = RT^2 \frac{\mathrm{d}\ln K_p^\ddagger}{\mathrm{d}T} \tag{4}$$

$$\Delta_\ddagger S_T^\circ = RT \frac{\mathrm{d}\ln K_p^\ddagger}{\mathrm{d}T} + R \ln K_p^\ddagger(T) \tag{5}$$

For an ideal gas at a standard state of $P^\circ = 1$ atm, the concentration of the standard state is given by P°/RT, and, when eq 1 is used, $\Delta_\ddagger S_T^\circ$ and $\Delta_\ddagger H_T^\circ$ can be expressed in terms of the reaction rate constant. For a bimolecular reaction ($\Delta n^\ddagger = -1$) we obtain

$$\Delta_\ddagger H_T^\circ = RT^2 \frac{\mathrm{d}\ln k^\ddagger}{\mathrm{d}T} - 2RT \tag{6}$$

$$\Delta_\ddagger S_T^\circ = \frac{\Delta_\ddagger H_T^\circ}{T} + R \ln \left[\frac{k^\ddagger(T) h P^\circ}{(k_B T)^2 N_A^{\,u}} \right] \tag{7}$$

where N_A is Avogadro's number and u is 1 for $k^\ddagger(T)$ in molar units and 0 for $k^\ddagger(T)$ in molecular units.

In many cases useful practical accuracy can be obtained by estimating $\Delta_\ddagger S_T^\circ$ and $\Delta_\ddagger H_T^\circ$ by group additivity and computing the rate constant from eq 1-3.[3] This is particularly appealing when conventional transition-state theory,[2,3] or variational transition-state theory[4-7] with a temperature-independent transition state, is accurate. In this case, the quasi-thermodynamic activation parameters may be interpreted in terms of the free energy (or enthalpy and entropy) change on passing to a single transition-state complex. For this interpretation the transition state is treated just like a bound, stable molecule except that 1 degree of freedom is missing, corresponding to the reaction coordinate; all the bound internal degrees of freedom can be analyzed in terms of their structure and vibrational frequencies. In many cases, however, this simple picture breaks down because the variational transition state depends on temperature or is not a good dynamical bottleneck, because of nonequilibrium effects, or because of quantal effects on reaction coordinate motion.[4-7] In such cases, if the rate constant is still represented by eq 1 and 2, $\Delta_\ddagger G_T^\circ$ cannot be calculated by statistical mechanics from the properties of a single transition-state complex, i.e., a single "substance". In the spirit of group additivity though, an attempt can be made to represent these effects by additional "group" contributions. We will call such contributions "nonsubstantial" contributions.

The rate constant can be expressed in terms of a transmission coefficient $\kappa(T)$, which includes the nonsubstantial contributions,

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and rate constant $k^{\mathrm{GTST}}(T, s)$ based on a single temperature-independent location s of the generalized transition state:

$$k(T) = \kappa(T)k^{\mathrm{GTST}}(T, s) \tag{8}$$

We introduce the factorizations

$$k^{\mathrm{GTST}}(T, s) = \frac{k_{\mathrm{B}}T}{h}(C^\circ)^{\Delta n^{\ddagger}} \exp(\Delta_s S_T^\circ/R) \exp(-\Delta_s H_T^\circ/RT) \tag{9}$$

and

$$\kappa(T) = \exp(\Delta_n S_T^\circ/R) \exp(-\Delta_n H_T^\circ/RT) \tag{10}$$

where $\Delta_s S_T^\circ$ and $\Delta_s H_T^\circ$ are substantial activation parameters obtained from the properties of a generalized transition state, "a substance", by expressions analogous to eq 4 and 5, and $\Delta_n S_T^\circ$ and $\Delta_n H_T^\circ$ are nonsubstantial activation parameters obtained from

$$\Delta_n H_T^\circ = RT^2 \frac{\mathrm{d} \ln \kappa}{\mathrm{d}T} \tag{11}$$

$$\Delta_n S_T^\circ = RT \frac{\mathrm{d} \ln \kappa}{\mathrm{d}T} + R \ln \kappa(T) \tag{12}$$

The nonsubstantial activation parameters $\Delta_n S_T^\circ$ and $\Delta_n H_T^\circ$ parametrize contributions from temperature-independent and temperature-dependent factors in the transmission coefficient, respectively. Since $\Delta_n S_T^\circ$ and $\Delta_n H_T^\circ$ are quasi-thermodynamic parameters, their temperature dependences are given by the usual formulas

$$\Delta_s S_T^\circ = \Delta_s S_{T_0}^\circ + \int_{T_0}^{T} (\Delta_s C_P^\circ/T)\, \mathrm{d}T \tag{13}$$

and

$$\Delta_s H_T^\circ = \Delta_s H_{T_0}^\circ + \int_{T_0}^{T} \Delta_s C_P^\circ\, \mathrm{d}T \tag{14}$$

where $\Delta_s C_P^\circ$ is the temperature-dependent substantial heat capacity of activation. The parameters $\Delta_n S_T^\circ$ and $\Delta_n H_T^\circ$ are purely phenomenological; however, because of their definition in eq 11 and 12, their temperature dependences can also be obtained from a single heat capacity analogue $\Delta_n C_P^\circ$ given by expressions analogous to eq 13 and 14. In this case the nonsubstantial heat capacity cannot be given the physical interpretation of the change in heat capacity of the molecular complex as it proceeds from reactants to the transition state, but it will be useful for providing a compact representation of the temperature dependence of both $\Delta_n S_T^\circ$ and $\Delta_n H_T^\circ$.

Table I. Activation Parameters for the Reaction $H + H_2 \rightarrow H_2 + H^a$

T, K	$\Delta_{\ddagger}H_T^\circ$	$\Delta_{\mathrm{var}}H_T^\circ$	$\Delta_{\mathrm{tun}}H_T^\circ$	$\Delta_{\ddagger}S_T^\circ$	$\Delta_{\mathrm{var}}S_T^\circ$	$\Delta_{\mathrm{tun}}S_T^\circ$
200	8.3	0.0	−4.0	−17.8	0.0	−10.2
300	7.8	0.0	−2.6	−19.6	0.0	−4.4
400	7.5	0.0	−1.9	−20.7	0.0	−2.3
600	6.9	0.0	−1.2	−21.8	0.0	−0.9
1000	6.3	0.0	−0.7	−22.6	0.0	−0.3
1500	6.0	0.0	−0.5	−22.9	0.0	−0.1

[a] Enthalpies in units of kcal mol^{-1}; entropies in units of cal mol^{-1} K^{-1}.

Estimates of the nonsubstantial activation parameters can be combined with estimates of the quasi-thermodynamic activation parameters to yield more accurate rate constants. In order to estimate the nonsubstantial contributions in the general case, it is useful to have some experience with their magnitude. In the present article we consider five reactions for which variational transition-state theory calculations[8-15] with transmission coefficients to account for quantal effects on the reaction coordinate motion provide rate constants in good agreement with experiment,[13,16-27] and we analyze the theoretical rate constants to obtain values for $\Delta_n S_T^\circ$, $\Delta_n H_T^\circ$, $\Delta_s S_T^\circ$, and $\Delta_s H_T^\circ$. The reactions considered are

$$\mathrm{H + H_2 \rightarrow H_2 + H} \tag{R1}$$

$$\mathrm{D + H_2 \rightarrow HD + H} \tag{R2}$$

$$\mathrm{H + D_2 \rightarrow HD + D} \tag{R3}$$

$$\mathrm{O(^3P) + H_2 \rightarrow OH + H} \tag{R4}$$

$$\mathrm{OH + H_2 \rightarrow H_2O + H} \tag{R5}$$

In these cases the largest contributions to the nonsubstantial activation parameters are due to tunneling.

2. Theory

We consider two factorizations of the total variational transition-state theory rate constant. The first allows a quantitative assessment of the improvement over conventional transition-state theory obtained by including the effects of variationally locating the transition state and the effects of quantum mechanical tunneling. This factorization is based upon the improved canonical variational theory[10] (ICVT) rate constant $k^{\mathrm{ICVT}}(T)$ with a semiclassical transmission coefficient[10,14,28-31] $\kappa_{\mathrm{tun}}(T)$ that accounts for quantal effects (tunneling and nonclassical reflection) on reaction coordinate motion

$$k(T) = \kappa_{\mathrm{tun}}(T)k^{\mathrm{ICVT}}(T) \tag{15}$$

$$k(T) = \kappa_{\mathrm{tun}}(T)\kappa_{\mathrm{var}}(T)k^{\ddagger}(T) \tag{16}$$

where $\kappa_{\mathrm{var}}(T)$ is defined by

$$\kappa_{\mathrm{var}}(T) = k^{\mathrm{ICVT}}(T)/k^{\ddagger}(T) \tag{17}$$

Both $\kappa_{\mathrm{var}}(T)$ and $\kappa_{\mathrm{tun}}(T)$ are parametrized as in eq 10 leading to the following expressions for the entropy and enthalpy of activation

$$\Delta_{\mathrm{a}}S_T^\circ = \Delta_{\mathrm{tun}}S_T^\circ + \Delta_{\mathrm{var}}S_T^\circ + \Delta_{\ddagger}S_T^\circ \tag{18}$$

$$\Delta_{\mathrm{a}}H_T^\circ = \Delta_{\mathrm{tun}}H_T^\circ + \Delta_{\mathrm{var}}H_T^\circ + \Delta_{\ddagger}H_T^\circ \tag{19}$$

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Table II. Activation Parameters for the Reaction D + H_2 → DH + H[a]

T, K	$\Delta_{\ddagger}H_T°$	$\Delta_{\mathrm{var}}H_T°$	$\Delta_{\mathrm{tun}}H_T°$	$\Delta_{\ddagger}S_T°$	$\Delta_{\mathrm{var}}S_T°$	$\Delta_{\mathrm{tun}}S_T°$
200	7.8	0.1	−3.5	−18.3	0.0	−9.1
300	7.3	0.1	−2.2	−20.1	0.0	−3.9
400	7.0	0.1	−1.6	−21.2	0.0	−2.1
600	6.5	0.1	−1.0	−22.2	0.0	−0.8
1000	6.0	0.0	−0.6	−22.8	−0.1	−0.2
1500	5.7	−0.1	−0.4	−23.1	−0.2	−0.1

[a] Enthalpies in units of kcal $\mathrm{mol^{-1}}$; entropies in units of cal $\mathrm{mol^{-1}\ K^{-1}}$.

Table III. Activation Parameters for the Reaction H + D_2 → HD + D[a]

T, K	$\Delta_{\ddagger}H_T°$	$\Delta_{\mathrm{var}}H_T°$	$\Delta_{\mathrm{tun}}H_T°$	$\Delta_{\ddagger}S_T°$	$\Delta_{\mathrm{var}}S_T°$	$\Delta_{\mathrm{tun}}S_T°$
200	9.0	0.1	−3.2	−18.9	0.0	−9.7
300	8.6	0.1	−1.7	−20.5	0.0	−3.2
400	8.3	0.1	−1.0	−21.4	0.0	−1.4
600	7.9	0.1	−0.6	−22.2	0.0	−0.5
1000	7.5	0.0	−0.3	−22.8	−0.1	−0.2
1500	7.0	−0.1	−0.2	−23.2	−0.1	−0.1

[a] Enthalpies in units of kcal $\mathrm{mol^{-1}}$; entropies in units of cal $\mathrm{mol^{-1}\ K^{-1}}$.

Table IV. Activation Parameters for the Reaction $O(^3P)$ + H_2 → OH + H[a]

T, K	$\Delta_{\ddagger}H_T°$	$\Delta_{\mathrm{var}}H_T°$	$\Delta_{\mathrm{tun}}H_T°$	$\Delta_{\ddagger}S_T°$	$\Delta_{\mathrm{var}}S_T°$	$\Delta_{\mathrm{tun}}S_T°$
200	9.5	0.2	−5.7	−19.6	0.0	−14.8
300	9.2	0.2	−4.2	−20.9	0.0	−8.9
400	8.9	0.2	−2.5	−21.7	0.0	−3.9
600	8.6	0.1	−1.1	−22.4	−0.1	−1.1
1000	8.2	0.0	−0.6	−22.9	−0.3	−0.3
1500	7.9	−0.3	−0.3	−23.1	−0.5	−0.1

[a] Enthalpies in units of kcal $\mathrm{mol^{-1}}$; entropies in units of cal $\mathrm{mol^{-1}\ K^{-1}}$.

Table V. Activation Parameters for the Reaction OH + H_2 → H_2O + H[a]

T, K	$\Delta_{\ddagger}H_T°$	$\Delta_{\mathrm{var}}H_T°$	$\Delta_{\mathrm{tun}}H_T°$	$\Delta_{\ddagger}S_T°$	$\Delta_{\mathrm{var}}S_T°$	$\Delta_{\mathrm{tun}}S_T°$
200	4.9	0.4	−4.4	−21.6	0.1	−10.1
300	4.4	0.4	−3.2	−23.5	0.2	−5.2
400	4.0	0.5	−2.5	−24.5	0.3	−3.0
600	3.6	0.4	−1.7	−25.4	0.2	−1.4
1000	3.4	0.3	−1.0	−25.6	0.0	−0.5
1500	3.6	0.1	−0.7	−25.5	−0.1	−0.2

[a] Enthalpies in units of kcal $\mathrm{mol^{-1}}$; entropies in units of cal $\mathrm{mol^{-1}\ K^{-1}}$.

Table VI. Activation Parameters for Five Reactions[a]

		reactions				
	T, K	H + H_2	D + H_2	H + D_2	O + H_2	OH + H_2
$\Delta_s H_T°$	200	8.3	7.8	9.1	9.7	5.3
	300	7.8	7.4	8.7	9.4	4.8
	400	7.5	7.0	8.4	9.1	4.4
	1500	6.0	5.6	7.0	7.8	3.8
$\Delta_n H_T°$	200	−4.0	−3.5	−3.2	−5.7	−4.4
	300	−2.6	−2.2	−1.7	−4.2	−3.2
	400	−1.9	−1.6	−1.0	−2.5	−2.5
	1500	−0.5	−0.5	−0.2	−0.5	−0.7
$\Delta_{\mathrm{therm}} H_T°$	200	0.0	0.0	0.0	0.0	0.0
	300	0.0	0.0	0.0	0.0	0.0
	400	0.0	0.0	0.0	0.0	0.0
	1500	0.0	0.0	0.1	−0.1	0.0
$\Delta_s S_T°$	200	−17.8	−18.3	−18.9	−19.6	−21.4
	300	−19.6	−20.1	−20.5	−20.9	−23.3
	400	−20.7	−21.1	−21.4	−21.7	−24.2
	1500	−22.9	−23.2	−23.3	−23.6	−25.5
$\Delta_n S_T°$	200	−10.2	−9.1	−9.7	−14.8	−10.1
	300	−4.4	−3.9	−3.2	−8.9	−5.2
	400	−2.3	−2.0	−1.4	−3.9	−3.1
	1500	−0.1	−0.1	−0.1	−0.2	−0.3
$\Delta_{\mathrm{therm}} S_T°$	200	0.0	0.0	0.0	0.0	0.0
	300	0.0	0.0	0.0	0.0	0.0
	400	0.0	0.0	0.0	0.0	0.0
	1500	0.0	0.0	0.0	−0.1	−0.1

[a] Enthalpies in units of kcal $\mathrm{mol^{-1}}$; entropies in units of cal $\mathrm{mol^{-1}\ K^{-1}}$.

where $\Delta_{\ddagger}S_T°$ and $\Delta_{\ddagger}H_T°$ are given by eq 6 and 7 and represent substantial contributions and $\Delta_{\mathrm{tun}}S_T°$, $\Delta_{\mathrm{tun}}H_T°$, $\Delta_{\mathrm{var}}S_T°$, and $\Delta_{\mathrm{var}}H_T°$ represent nonsubstantial contributions.

The second factorization attempts to maximize the substantial contributions to the enthalpy and entropy while minimizing the nonsubstantial contributions by basing the substantial part on a single temperature-independent transition state located at the maximum of the adiabatic ground-state potential curve[10] (the variational transition state at 0 K) instead of the conventional transition state at the saddle point. We write

$$k^{\mathrm{ICVT}}(T) = \kappa_{\mathrm{therm}}(T)k^{\mathrm{GTST}}(T, s_{\ddagger}^{\mathrm{AG}}) \tag{20}$$

where $s = s_{\ddagger}^{\mathrm{AG}}$ denotes the location of the adiabatic ground-state maximum and $\kappa_{\mathrm{therm}}(T)$ accounts for finite-temperature deviations due to the temperature dependence of the improved canonical variational transition state. Analysis of $k^{\mathrm{GTST}}(T, s_{\ddagger}^{\mathrm{AG}})$ by eq 9 yields $\Delta_s S_T°$ and $\Delta_s H_T°$, and analysis of eq 15 and 20 yields

$$\Delta_n S_T° = \Delta_{\mathrm{tun}}S_T° + \Delta_{\mathrm{therm}}S_T° \tag{21}$$

$$\Delta_n H_T° = \Delta_{\mathrm{tun}}H_T° + \Delta_{\mathrm{therm}}H_T° \tag{22}$$

In all cases we used ab initio potential energy surfaces, namely the surface of Liu, Siegbahn, one of the authors, and Horowitz[32-34] for reactions R1–R3, a surface called M2[12] based on the modified[35] polarization configuration interaction calculations of Walch et al.[36-38] for reaction R4, and the Walch–Dunning–Schatz–Elgersma surface[39,40] for reaction R5.

For reactions R1–R4, $\kappa_{\mathrm{tun}}(T)$ is approximated by the least action ground-state (LAG) method.[31] In these cases all geometries along the minimum energy paths are collinear, stretching anharmonicity is included by the WKB approximation[41] for the ground state and the Morse I approximation[42] for excited states, and bending anharmonicity is included by a quadratic–quartic approximation.[43,44] For reaction R5, $\kappa_{\mathrm{tun}}(T)$ is approximated by the small-curvature semiclassical adiabatic ground-state (SCSAG) approximation.[14,28-31] For this reaction all geometries along the minimum energy path are coplanar, anharmonicity is included by the independent-normal-mode approximation[6,14] with the Morse III approximation[14] for in-plane vibrations and a quadratic–quartic approximation[6] for out-of-plane bends.

3. Results and Discussion

Tables I–V show results of the factorization of the activation parameters into contributions from conventional TST, variational effects, and tunneling effects for the five reactions over a range of temperatures from 200 to 1500 K. Table VI summarizes the results of the factorization into substantial and nonsubstantial contributions at four selected temperatures for all five reactions. The deviations of the VTST values from GTST values calculated at the 0 K transition state are also shown for reference. Table VII provides a compact presentation of the substantial and nonsubstantial contributions to the activation parameters for the five reactions in terms of the heat capacities of activation.

The nonsubstantial contributions (primarily from tunneling) to both the enthalpy and entropy of activation are seen to be quite large. For the systems studied here the classical barriers are fairly

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Table VII. Activation Parameters for Five Reactions[a]

reaction	contribution	$\Delta H_T°$ (T = 300 K)	$\Delta S_T°$ (T = 300 K)	$\Delta C_T°$					
				200	300	400	600	1000	1500
$H + H_2$	substantial	7.8	−19.6	−4.9	−4.2	−3.4	−2.1	−1.1	−1.0
	nonsubstantial	−2.6	−4.4	20.8	9.4	5.3	2.1	0.6	0.3
$D + H_2$	substantial	7.4	−20.1	−4.8	−4.0	−3.2	−2.0	−1.1	−1.0
	nonsubstantial	−2.2	−3.9	18.7	8.5	4.7	1.9	0.5	0.1
$H + D_2$	substantial	8.7	−20.5	−4.6	−3.5	−2.7	−1.7	−1.1	−1.0
	nonsubstantial	−1.7	−3.2	23.2	9.5	3.9	1.3	0.3	0.1
$O + H_2$	substantial	9.4	−20.9	−3.5	−3.0	−2.5	−1.7	−1.0	−0.6
	nonsubstantial	−4.2	−8.9	9.0	19.2	12.8	3.2	0.6	0.0
$OH + H_2$	substantial	4.8	−23.3	−5.4	−3.9	−2.8	−1.5	−0.3	0.5
	nonsubstantial	−3.2	−5.2	13.2	9.6	5.8	2.6	1.0	0.6

[a] Enthalpies in units of kcal mol^{-1}; entropies and heat capacities in units of cal mol^{-1} K^{-1}.

high (9.8 kcal/mol for $H + H_2$ and isotopic analogues, 12.6 kcal/mol for $O + H_2$, and 6.1 kcal/mol for $OH + H_2$), which favors locating the variational dividing surface close to the saddle point. Therefore, the variational contributions to the enthalpy and entropy of activation are generally small; they are largest for the reaction with the smallest barrier, $OH + H_2$, where they contribute up to 0.5 kcal/mol to the enthalpy of activation and 3 cal mol^{-1} K^{-1} to the entropy of activation. The high barriers also lead to considerable tunneling at low temperatures. This is reflected in the large contributions to the enthalpies and entropies of activation at temperatures of about 600 K and lower. Tunneling effectively lowers the threshold for reaction below the classical threshold, and thereby makes a negative contribution to the enthalpy of activation. Thus, since tunneling decreases with increasing temperature, $\Delta_{\mathrm{tun}}H_T°$ also increases (becomes less negative). We see a similar trend for the entropy of activation; $\Delta_{\mathrm{tun}}S_T°$ is consistently less than zero but decreases in magnitude for increasing temperature.

Table VI shows that most of the effect of variationally optimizing the location of the transition-state dividing surface at each temperature can be obtained by placing the transition-state dividing surface at a single temperature-independent location, the maximum of the ground-state adiabatic curve ($s = s_{\ddagger}^{AG}$). A measure of the importance of placing the dividing surface at a location different than $s_{\ddagger}^{AG}$ is provided by $\Delta_{\mathrm{therm}}S_T°$ and $\Delta_{\mathrm{therm}}H_T°$, which are both small; these quantities vary from −0.1 to 0.0 cal mol^{-1} K^{-1} and from −0.1 to 0.1 kcal/mol, respectively, for all five reactions from 200 to 1500 K. The effect of the variational contributions in Tables I–V are approximately combined with the conventional TST contributions to give the substantial contributions in Table VI (e.g., $\Delta_s H_T° \approx \Delta_{\ddagger}H_T° + \Delta_{\mathrm{var}}H_T°$), and the nonsubstantial contributions are dominated by the tunneling contributions.

Another interesting trend seen in Tables I–V is that $\Delta_{\ddagger}H_T°$ monotonically decreases with increasing temperature for all reactions. From eq 6 we see that if $\ln k^{\ddagger}(T)$ varies linearly with $1/T$, then $\Delta_{\ddagger}H_T°$ will decrease with temperature from the $-2RT$ term. At the low temperature the decrease is approximately the same as for $-2RT$, but at higher temperatures the curvature of $\ln k^{\ddagger}(T)$ becomes larger and $\Delta_{\ddagger}H_T°$ decreases less rapidly. Because the variational contributions are small, this trend is also reflected in the substantial enthalpy of activation seen in Table VI. Also, as noted above, the nonsubstantial contributions have the same trends as the tunneling contributions. Because tunneling is so important at the lower temperatures, the total enthalpy of activation (substantial plus nonsubstantial) increases with increasing temperature for all five reactions at the lowest few temperatures. For all systems except $OH + H_2$ this trend reverses at higher T so that the total enthalpy of activation does not have a monotonic dependence on the temperature.

These trends are also exhibited in the heat capacities shown in Table VII. We see that for all five reactions the substantial contributions to the heat capacity of activation are negative and the nonsubstantial contributions are positive. At low temperature ($T \leq 400$ K) the magnitude of the nonsubstantial contributions to $\Delta C_P°$ are larger than those of the substantial contributions, leading to a net increase in both $\Delta_a S_T°$ and $\Delta_a H_T°$ at higher temperatures. For all reactions except the $OH + H_2$ reaction the magnitude of the substantial contributions to $\Delta C_P°$ becomes larger at temperatures above 600 K, and both $\Delta_a S_T°$ and $\Delta_a H_T°$ decrease with further increases in T.

It is typical to write the rate constant in Arrhenius form

$$k(T) = A(T)\exp[-E_a(T)/k_B T] \qquad (23)$$

and express the Arrhenius parameters in terms of the enthalpy and entropy of activation. From the Tolman definition[45–47] of the activation energy, we obtain

$$E_a(T) = \Delta_s H_T° + \Delta_n H_T° + 2RT \qquad (24)$$

and using eq 8–10, 23, and 24, we obtain

$$\ln A(T) = \ln\left[\frac{(k_B T)^2 N_A{}^u}{hP°}\right] + \frac{\Delta_s S_T° + \Delta_n S_T°}{R} + 2 \qquad (25)$$

For all five reactions studied here, the substantial contributions to the activation energy are nearly constant at low temperature, changing by less than 0.2 kcal/mol from 200 to 400 K. However, because of the importance of tunneling at low temperature, the total activation energies are greatly decreased at these lower temperature—by as much as 5.7 kcal/mol at 200 K for the $O + H_2$ reaction—and the activation energy changes significantly over the entire temperature range. For example, the activation energy for the $O + H_2$ reaction is 4.8, 6.4, 8.2, 9.9, 11.6, and 13.3 kcal/mol at 200, 300, 400, 600, 100, and 1500 K, respectively. Similarly, the change in the entropy of activation with temperature and the explicit temperature dependence in eq 25 lead to a change in $A(T)$ for this reaction of 4 orders of magnitude from 200 to 1500 K. The nonsubstantial contributions to the quasi-thermodynamic properties account for these significant non-Arrhenius effects.

Using estimates of the contributions to the conventional TST entropy of activation based on group additivity relationships, Benson[3] has approximated the Arrhenius A factor for the $H + D_2$ reaction; an estimate for $\Delta_{\ddagger}S_{300}°$ of −18.7 cal mol^{-1} K^{-1} yielded $A_{300} = 10^{-9.8}$ cm^3 molecule^{-1} s^{-1}. The estimate of $\Delta_{\ddagger}S_{300}°$ is slightly higher than our computed value of −20.6 cal mol^{-1} K^{-1} but neglects the contribution of −3.2 cal mol^{-1} from tunneling. Combining the substantial and nonsubstantial contributions yields our computed value of $A_T = 10^{-10.9}$ cm^3 molecule^{-1} s^{-1}. Our results show that tunneling contributions can change the Arrhenius A factor by over 1 order of magnitude at low temperatures. Benson's estimate of the Arrhenius A factor at 300 K is in better agreement with our computed value at 1000 K ($10^{-9.6}$ cm^3 molecule^{-1} s^{-1}), where tunneling contributions are less than 30%.

4. Conclusions

A new partitioning of the phenomenological enthalpy and entropy of activation into substantial and nonsubstantial contributions

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has been presented. The former are obtained from the properties of a single temperature-independent transition state (a "substance") by conventional methods. The nonsubstantial contributions are obtained from more global properties of the potential energy surface (including the dependence of the variational transition state on temperature and quantum mechanical tunneling effects). An analysis of these contributions has been performed for five reactions for which the potential energy surface is known to give computed rate constants in excellent agreement with experiment. This analysis shows that the nonsubstantial contributions can be very significant; for example, for the OH + H_2 reaction the substantial and nonsubstantial contributions to the enthalpy of activation at 300 K are 4.8 and −3.8 kcal/mol, respectively, and for the O + H_2 reaction the substantial and nonsubstantial contributions to the entropy of activation at 300 K are −20.9 and −8.9 cal mol^{-1} K^{-1}, respectively, for a standard state of 1 atm.

All the reactions studied here are hydrogen (or deuterium) atom transfer reactions with fairly high barriers (6–13 kcal/mol). For these reactions the nonsubstantial contributions are predominantly from quantum mechanical tunneling and the effect of variationally optimizing the location of the transition-state dividing surface is small. For reactions with smaller barriers we expect the effect of quantum mechanical tunneling to be smaller, but for those reactions the effects of variationally locating the dividing surface will become more important especially at higher temperatures.[48,49] It is therefore expected that the nonsubstantial contributions will be significant for a wide range of gas-phase chemical reactions.

The temperature dependence of both the substantial and nonsubstantial contributions to both the enthalpy and entropy of activation can be expressed in terms of temperature-dependent heat capacities of activation. This allows both contributions to the enthalpy and entropy of activation to be compactly tabulated in terms of their values at a single temperature (e.g., room temperature) and the temperature dependence given by the heat capacity of activation at several temperatures. This provides the basis for establishing a semiempirical data base, which includes important variational and tunneling effects in a thermochemical kinetic model.

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Registry No. H, 12385-13-6; D, 16873-17-9; O, 17778-80-2; OH, 3352-57-6; H_2, 1333-74-0; D_2, 7782-39-0.

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Transition Structures for the Allylboration Reactions of Formaldehyde by Allylborane and Allylboronic Acid

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Abstract: Chair and twist-boat transition structures for the reactions of formaldehyde with allylborane and allylboronic acid have been located with ab initio molecular orbital calculations and the 3-21G basis set. The relative energies of the transition structures were evaluated with the 6-31G* basis set. The twist-boat transition structure is predicted to be 8 kcal/mol less stable than the chair.

The stereocontrolled formation of carbon–carbon bonds is of great importance in organic synthesis.[1] Additions of allylic organometallic reagents to carbonyl compounds have been actively explored in recent years,[2,3] and the use of allylic organoborane reagents, in particular, has been shown to be a valuable method for the construction of carbon–carbon bonds with excellent control of stereochemistry.[3-5]

Allylic boranes and boronic esters undergo rapid reactions with carbonyl compounds. The products of these reactions arise from transfer of the rearranged allylic group from the metal to the carbonyl carbon (S_E2' reaction). These products can then be easily converted into homoallylic alcohols or aldols, making this approach

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