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Microcanonical Modeling of the Thermokinetic Method[†]

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A microcanonical analysis of the thermokinetic method is performed using statistical rate calculations based on orbiting transition state theory in order to model a proton transfer process: $MH^+ + B_i \rightarrow M + B_iH^+$. The reaction efficiency is calculated as a function of the difference in zero point energy of reactants and products. Several models of reactions were investigated in order to simulate situations where the base of interest M exhibits loss of entropy upon protonation of up to ∼40 J mol^{-1} K^{-1}. It is shown that the standard thermokinetic method would predict correct 298 K gas phase basicities, $GB_{298}(M)$, even for polydentate molecules M, if experiments are conducted at this temperature. Proton affinity, $PA_{298}(M)$, and protonation entropy may be obtained by the thermokinetic method only in special circumstances such as, for example, experiments conducted at various temperatures.

Introduction

The gas phase basicity, GB(M), and the proton affinity, PA(M), of a molecule M are most commonly obtained by studying proton transfer reactions involving the base of interest M and reference compounds B_i:

$$MH^+ + B_i \rightarrow M + B_iH^+$$

Various techniques and methods have been designed to attain these thermochemical quantities.[1,2] One of them, the "thermokinetic method", is based on a correlation between the bimolecular rate of the above reaction and the corresponding standard free energy change $\Delta_i G°$.[3] The basis of the method is to consider that a proton transfer from MH^+ to B_i (reaction 1) occurs via a single reaction intermediate $[MHB_i]^+$:

$$MH^+ + B_i \underset{k_{-1}}{\overset{k_{coll}}{\rightleftarrows}} [MHB_i]^+ \xrightarrow{k_1} M + B_iH^+ \tag{1}$$

Thus, applying the steady-state approximation to this intermediate, the reaction efficiency RE, i.e., the ratio of the experimental rate constant, k_{exp}, determined from the MH^+ decay, to the collision rate constant, k_{coll}, can be expressed by eq 2:

$$RE = k_{exp}/k_{coll} = [1 + k_{-1}/k_1)]^{-1} \tag{2}$$

where k_{-1} and k_1 are unimolecular rate constants for the backward and forward dissociations of the intermediate ion $[MHB_i]^+$ (see eq 1).

By using the canonical thermodynamic formulation of the transition state theory, the reaction efficiency becomes

$$RE = [1 + \exp((\Delta_i G^{\ddagger}_T)/RT)]^{-1} \tag{3}$$

with $\Delta_i G^{\ddagger}_T$ being the difference in Gibbs free energy between the transition state of the two dissociation channels, i.e., $\Delta_i G^{\ddagger}_T = G^{\ddagger\circ}_T\,([MHB_i]^+ \rightarrow M + B_iH^+) - G^{\ddagger\circ}_T\,([MHB_i]^+ \rightarrow MH^+ + B_i)$ at temperature T. If these transition states are close (in energy and in structure) to the corresponding final states, eq 3 may be simplified to

$$RE = [1 + \exp((\Delta_i G°_T)/RT)]^{-1} \tag{4}$$

with

$$\Delta_i G°_T = G°_T(M) + G°_T(B_iH^+) - G°_T(MH^+) - G°_T(B_i)$$

Using the thermokinetic method consists of deducing the gas phase basicity $GB_{298}(M)$ by plotting experimental RE values obtained for a series of reaction 1 involving bases B_i of known basicities, as a function of $GB_{298}(B_i)$, and by fitting the data with a parametric function of the type

$$RE = a/[1 + \exp(b(c - GB_{298}(B_i))] \tag{5}$$

where a is a normalizing factor, b the slope of the curve at RE = 0.5, and c is the position of the point RE = 0.5 on a GB scale, these two latter correlation parameters being theoretically related to $1/RT$ and $GB_{298}(M)$, respectively.

In the original development of the thermokinetic method,[3] $\Delta_i G^{\ddagger}_T$ (eq 3) has been written as

$$\Delta_i G^{\ddagger}_T = GB_{298}(M) - GB_{298}(B_i) + \Delta G°_a$$

with $\Delta G°_a$ being a correction term including (i) the possible differences in Gibbs free energy between transition states and separated species and (ii) the Gibbs free energy change from 298 K to T. Several series of experiments have shown that the $\Delta G°_a$ correction may be assimilated to RT, and a number of gas phase basicity values were determined using this approximation. It must be emphasized, however, that the proton transfer reactions involved in these different studies were associated with a negligible entropy variation (i.e., $\Delta_i S°_{298} <$ 10 J mol^{-1} K^{-1}). It is therefore of interest to examine the applicability of the thermokinetic method in more general situations. The main goal of the present study is thus to control the validity of the method to effectively predict $GB_{298}(M)$ values,

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TABLE 1: Summary of the Parameters Used in the Orbiting Transition State Theory Calculations

M (B) Models I, II, III (Number of Frequencies Doubled for Models IV−VII)	
rotational constants (GHz)	10.091, 8.450, 4.877
frequencies (cm^{-1})	3170(2), 3100(2), 3050(2), 1820, 1510(2), 1490(2), 1410(2), 1240, 1130, 1100, 900(2), 790, 530, 490, 380, 140, 60
polarizability (Å^3)	6.33
MH$^+$ (BH$^+$) Models I, II, III (Number of Frequencies Doubled for Models IV−VII)	
rotational constants (GHz)	9.767, 8.311, 4.753
frequencies (cm^{-1})	3600, 3190, 3160, 3120, 3110, 3030, 3020, 1610, 1500, 1490, 1470, 1450, 1430, 1400, 1390, 1170, 1110, 1090, 960, 940, 830, 730, 510, 480, 390, 120, 100
Complex MHB$^+$ Models I, II, III (Number of Frequencies Doubled for Models IV−VII)	
rotational constants (GHz)	4.334, 0.760, 0.658
frequencies (cm^{-1})	3190(2), 3180, 3170, 3120(3), 3110, 3060(2), 3050(2), 1760, 1700, 1640, 1510, 1500(2), 1490, 1480(2), 1470(2), 1430, 1420(3), 1310, 1290(2), 1150, 1130(2), 1110, 1050, 940(2), 900, 890, 830, 800, 610, 520, 500, 490, 410, 380, 250, 160, 140, 120, 110, 100, 90, 60, 40, 30

Frequencies (cm^{-1}) of the Dissociation Products Changed in the Various Models

model	initial values in the set of frequencies	values used
I, IV	none	none
II	100	300
	120	360
III	60	180
	100	300
	120	360
	140	420
V	60(2)	120(2)
VI	60(2)	120(2)
	140(2)	280(2)
VII	60(2)	120(2)
	140(2)	280(2)
	280(2)	760(2)
	490(2)	980(2)

particularly when noticeable entropy change is occurring during the proton transfer reaction 1.

For this purpose, statistical rate calculations are introduced to evaluate reaction efficiencies RE (eq 2) for model systems of known thermochemistry. Accordingly, the transient intermediate $[MHB_i]^+$ appearing in eq 1 is an internally excited species which may dissociate unimolecularly to give either M + B_iH^+ or MH^+ + B_i with rate coefficients k_1 and k_{-1}. In such a situation, another means to express the dissociation rates k_1 and k_{-1} consists of using the microcanonical formulation of the unimolecular rate constants:

$$k(E,E_0) = \sum P^{\ddagger}(E-E_0)/hN(E) \qquad (6)$$

where $\sum P^{\ddagger}(E-E_0)$ is the sum of states of the transition structure with a total energy $E - E_0$, $N(E)$ is the density of states of the intermediate $[MHB_i]^+$ at an internal energy E, and h is the Planck constant. Most probably, the $[MHB_i]^+$ intermediate involved during a proton transfer process consists of proton bound species, thus, the dissociation rates k_1 and k_{-1} should be more properly expressed using a formulation based on orbiting transition state theory. Accordingly, this theory takes into account the long range ion/induced dipole potential occurring in the product region of barrierless dissociations such as those occurring from a proton bound intermediate $[MHB_i]^+$. As a consequence, since the transition state configuration consists of the two separating species interacting by the above-mentioned potential, a comparison of the kinetic results with the classical thermochemical properties of the separated products may be directly done. A comparable approach has proven suitable during a recent assessment of the kinetic method.[4]

Methods

Two sets of systems were chosen to model $[MHB_i]^+$ and its dissociation products (eq 1). The first set (models I, II, and III) consists of $[MHB_i]^+$ species containing 57 oscillators, and M (or B_i) and MH^+ (or B_i H^+) containing 24 and 27 oscillators. The second set (models IV, V, VI, and VII) includes $[MHB_i]^+$ intermediates containing 108 oscillators, and M (or B_i) and MH^+ (or B_i H^+) containing 48 and 54 oscillators. The exact values of the harmonic vibrational frequencies as well as the moment of inertia and polarizabilities necessary to calculate the sum and densities of states (Table 1) were derived from the proton bound acetone dimer and its dissociation products.[4]

Models I and IV were constructed to simulate reaction 1 occurring without entropy change. By contrast, models II, III, V, VI, and VII were constructed in order to mimic reactions 1 associated with significant entropy changes such as that occurring when M is a polydentate molecule. In those cases, the vibrational frequencies of M and their protonated forms MH^+ have been obtained by changing several harmonic frequencies in order to account for the hindrance of several rotations after protonation. Microcanonical rate constant calculations were performed in the framework of the statistical phase space theory using the TSTPST package elaborated by Chesnavich et al..[5] The sum and density of states are calculated using the Beyer−Swinehart algorithm[6] with vibrational degrees of freedom, including hindered rotations, treated as harmonic oscillators.

The entropies and enthalpies associated with the various models were calculated by standard statistical thermodynamic formulas[7] using the same parameters as those used in the rate constant calculations, i.e., those listed in Table 1.

A nonlinear iterative least-squares procedure has been used to solve parametric equations relating reaction efficiency, RE, to thermochemical quantities [eq 5] (Levenberg−Marquard algorithm implemented in the IGOR Pro package, Wavemetrics Inc).

The following constant and conversion factor values were used throughout this paper: $R = 8.31451$ J K^{-1} mol^{-1} = 8.617 385 10^{-5} eV K^{-1}; 1 eV = 96.4853 kJ mol^{-1}.

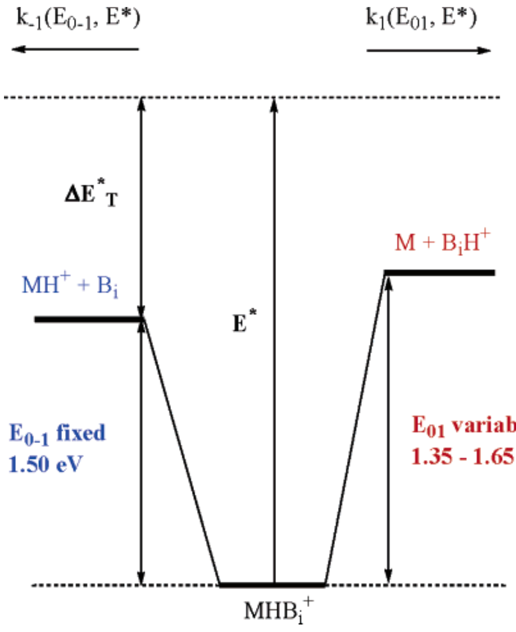

Figure 1. Schematic zero point energy diagram and definitions of the energies used in the calculations of the rate constants k_1 and k_{-1}.

Results and Discussion

Thermokinetic Modeling. Competitive dissociations of the reaction intermediate $[MHB_i]^+$ into $MH^+ + B_i$ (k_{-1}) and $M + B_iH^+$ (k_1) were examined through seven models. Models I and IV consider two reactions leading to products differing only by their 0 K energies. The same set of parameters are thus used for both channels. This model idealizes the case where M and B_i are "structurally similar" molecules (e.g., simple monodentate bases), a situation expected to be associated with negligible entropy difference $\Delta_iS°$. By contrast, models II, III, V, VI, and VII aim to mimic reactions between a polydentate base M and a series of monodentate bases B_i where, that time, $\Delta_iS°$ is expected to be positive. Again, reactants $MH^+ + B_i$ and products $M + B_iH^+$ differ by their 0 K energies, but also by some of their low frequency vibrational modes. During protonation of a polydentate base, a strong intramolecular hydrogen bond is generally created in the MH^+ ions and induces a hindering effect on several torsional modes thus increasing the corresponding rotational energy barriers. For example, the rotational barriers associated with C−C, C−O, or C−N bonds in α,ω diols,[8a] diamines,[8b] and amino alcohols[8c] are increased of by a factor of 5−10 when passing from the neutral to the protonated forms. This corresponds to a change in the corresponding vibrational frequencies by a factor of 2−3 for each hindered rotation. Consequently, models II, III, V, VI, and VII were designed by increasing by a factor of 2 or 3 several low frequencies of $MH^+ + B_i$ with respect to that of $M + B_iH^+$ (see Table 1).

For all the models, calculation of the rate constants k_1 and k_{-1} has been done assuming a series of proton transfer reactions between an ion MH^+ of interest and several reference bases B_i. The critical energy for dissociation of the intermediate MHB_i^+ into $MH^+ + B_i$, E_{0-1}, is taken constant and equal to 1.50 eV while the critical energy for dissociation into $M + B_iH^+$, E_{01}, varies between 1.35 and 1.65 eV by steps of 0.05 eV (Figure 1). The energy domain, of ca. 30 kJ mol^{-1}, corresponds roughly to the range of the GB(M) − GB(B_i) differences used during the practical determination of GB(M) through eq 5 by the thermokinetic method.[3,8]

TABLE 2: Vibrational Contributions and Overall Average Energies[a] of Reactants $MH^+ + B$ Available for Reaction at Temperature T for Models I−VII

T (K)	model	$\langle E_{vib}\rangle_T$ [b] (eV)	ΔE^*_T (eV)
298	I	0.148	0.264
	II	0.141	0.257
	III	0.132	0.248
	IV	0.288	0.404
	V	0.285	0.401
	VI	0.273	0.389
	VII	0.242	0.358
500	I	0.412	0.625
	II	0.404	0.617
	III	0.390	0.603
	IV	0.828	1.041
	V	0.822	1.035
	VI	0.809	1.022
	VII	0.757	0.970
1000	I	1.619	2.007
	II	1.597	1.985
	III	1.574	1.962
	IV	3.233	3.621
	V	3.227	3.615
	VI	3.211	3.599
	VII	3.136	3.524

[a] Expressed in eV (1 eV = 96.4853 kJ mol^{-1}). [b] Calculated using a thermal distribution given by $N(E)$ exp($-E/RT$), the density of vibrational states $N(E)$ being calculated by exact count of the vibrational states.

The main point of the modeling is to define the internal energy content of the intermediate ions MHB_i^+ which corresponds, as closely as possible, to experimental situations. This quantity, called E^* in Figure 1, is the sum of the critical energy for the backward reaction, E_{0-1}, and a nonfixed excess energy ΔE^*_T. So far, the thermokinetic method has been applied to the determination of gas phase basicities from Fourier transform ion cyclotron resonance (FT-ICR) and flowing afterglow (FA) or selected ion flow tube (SIFT) experimental rates.[3,9] During these experiments, the reactants are thermalized by collision with a buffer gas and then allowed to react at variable reaction times. The average energy of the reactants MH^+ and B_i available for reaction at temperature T, ΔE^*_T, may be considered to be the sum of translational, rotational, and vibrational contributions:

$$\Delta E^*_T = \langle E_{trans}\rangle_T + \langle E_{rot}\rangle_T + \langle E_{vib}\rangle_T \qquad (7)$$

The translational energy which may eventually be converted into internal energy is approximated here by the average center of mass kinetic energy (3/2)RT. Similarly, the rotational terms $\langle E_{rot}\rangle_T$ are equal to (3/2)RT for both species. Finally, the term $\langle E_{vib}\rangle_T$ should be calculated over a Maxwell−Boltzmann distribution of internal energy of the reactants. A summary of the values of $\langle E_{vib}\rangle_T$ and ΔE^*_T is given in Table 2 for the considered systems. Usually, FT-ICR, FA, and SIFT experiments are conducted at temperatures close to 298 K. However, as it will be seen later, examination of the temperature effect is of interest and thus contributions to ΔE^*_T at 500 and 1000 K are also given in Table 2.

For each model, the ratio of rate coefficients $k_{-1}(E^*,E_{0-1})/k_1(E^*,E_{01})$ has been calculated for the various E_{01} values (E_{0-1} being fixed to 1.5 eV) and with temperature of the reactants equal to 298, 500, and 1000 K. The results of the simulation are illustrated by plotting the reaction efficiencies RE = $[1 + k_{-1}/k_1)]^{-1}$ (eq 2) as a function of the critical energy difference $\Delta_iE° = E_{01} - E_{0-1}$ (Figures 2 and 3). The data points were then fitted by a parametric function of the type

$$RE_{fit} = a/[1 + \exp(b(\Delta_iE° + d)] \qquad (8)$$

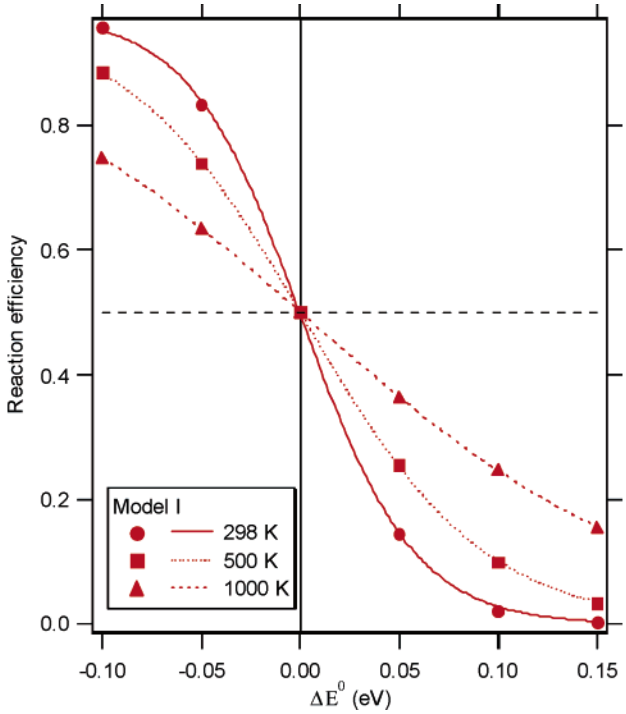

Figure 2. Thermokinetic plot for the reaction $MH^+ + B_i \rightarrow M + B_iH^+$ assumed to proceed without entropy change ($\Delta_iS°_T = 0$) at reactant temperature of 298, 500, and 1000 K (model I).

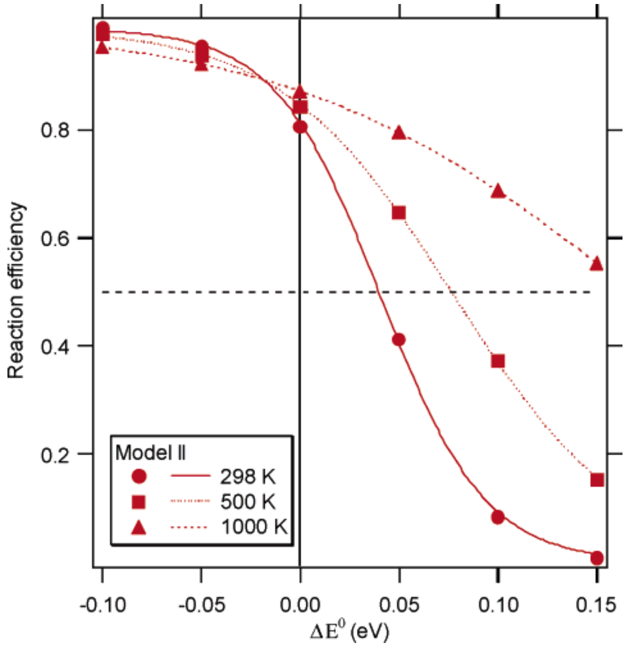

Figure 3. Thermokinetic plot for the reaction $MH^+ + B_i \rightarrow M + B_iH^+$ assumed to proceed with an entropy change $\Delta_iS°_{298}$ equal to 17 J mol^{-1} K^{-1} (model II).

using a nonlinear iterative least-squares procedure. Figures 2, 3, and 4 include the RE calculated from eq 2 and the RE_{fit} curves obtained for the various model reactions at temperatures T = 298, 500, and 1000 K. The values of the corresponding fitting parameters *a*, *b*, and *d* are gathered in Table 3.

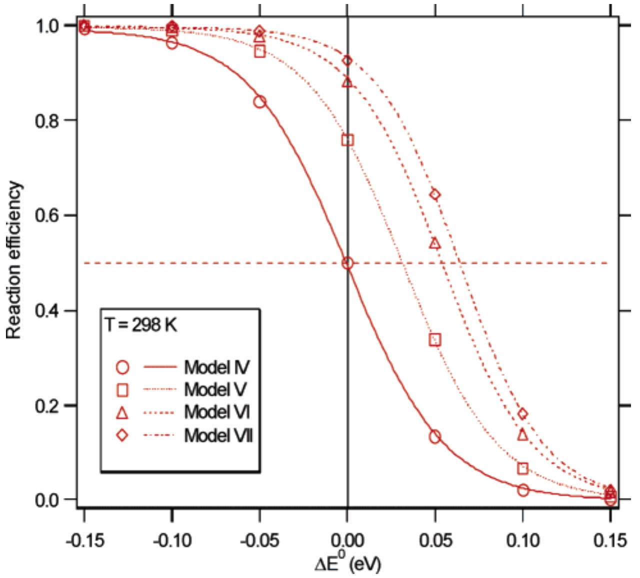

Figure 4. Thermokinetic plot for the reaction $MH^+ + B_i \rightarrow M + B_iH^+$ assumed to proceed at 298 K reactant temperature with entropy change $\Delta_iS°_{298}$ ranging from 0 to 34 J mol^{-1} K^{-1} (models IV, V, VI, VII).

TABLE 3: Results of the Thermokinetic Fitting: Temperature *T* of the Reactants and Parameters *a*, *b*, *d* (± Standard Deviation)

model	T	a	b (eV^{-1})	d (meV)
I	298	0.978 ± 0.009	35.4 ± 1.0	−0.8 ± 1.0
	500	0.974 ± 0.007	22.0 ± 0.3	−2.2 ± 1.0
	1000	0.974 ± 0.004	11.39 ± 0.05	−4.7 ± 0.8
II	298	0.987 ± 0.009	38.0 ± 1.4	−40.4 ± 1.1
	500	0.990 ± 0.004	22.9 ± 0.3	−77.3 ± 0.7
	1000	0.995 ± 0.001	11.55 ± 0.04	−169.3 ± 0.2
III	298	0.992 ± 0.007	43.2 ± 1.4	−76.2 ± 1.0
	500	0.997 ± 0.001	24.1 ± 0.3	−148.0 ± 0.3
	1000	0.9992 ± 0.0001	11.65 ± 0.04	−334.0 ± 0.6
IV	298	0.991 ± 0.006	35.8 ± 0.9	0.4 ± 0.9
	500	0.992 ± 0.003	22.1 ± 0.2	−0.5 ± 0.4
	1000	0.990 ± 0.002	11.40 ± 0.03	−1.7 ± 0.3
V	298	0.995 ± 0.003	37.0 ± 0.6	−31.6 ± 0.5
	500	0.995 ± 0.002	22.7 ± 0.2	−55.5 ± 0.4
	1000	0.996 ± 0.001	11.46 ± 0.03	−115.3 ± 0.1
VI	298	0.9956 ± 0.003	38.94 ± 0.73	−54.0 ± 0.5
	500	0.997 ± 0.001	23.1 ± 0.2	−100.7 ± 0.3
	1000	0.9987 ± 0.0002	11.51 ± 0.02	−219.3 ± 0.2
VII	298	0.996 ± 0.003	41.68 ± 0.72	−64.1 ± 0.5
	500	0.998 ± 0.001	24.0 ± 0.1	−142.0 ± 0.2
	1000	0.9998 ± 0.0004	11.67 ± 0.02	−364.0 ± 0.4

In models I and IV, reactant and products are supposed to be identical and thus $k_1 = k_{-1}$ at all energies when $\Delta_iE° = 0$, an equality leading, obviously, to RE = 0.5. Data given in Table 3 and illustrated by the thermokinetic plot shown in Figure 2 in the case of model I confirm this expectation. For the three temperatures T considered, the sigmoid curves intercept the RE = 0.5 line near to $\Delta_iE° = 0$. The parameter *d* (Table 3), which according to eq 8 represents the shift of this intercept on the energy axis, is really close to zero; its maximum deviation is less than 5 meV (0.5 kJ mol^{-1}).

The results given by the simulation using model II, are displayed in Figure 3. The graphs clearly show the profound effect of the temperature T upon RE. By comparison with Figure 2, Figure 3 shows that the increase in T is associated not only with a change in slope but also with a shift of the intercept of the curves with the RE = 0.5 line. This is reflected by the values of the fitting parameters *b* and *d* in Table 3.

Thermochemistry. In order to compare results given by the microcanonical modeling, which relate RE to $\Delta_iE°$, and the canonical expression, which relate RE to the Gibbs free energy of reaction 1 at temperature T, $\Delta_iG°_T$, it is obviously necessary to relate $\Delta_iG°_T$ to $\Delta_iE°$.

The difference in zero point thermodynamic energy $\Delta_i E^\circ$ used in the microcanonical modeling is given by

$$\Delta_i E^\circ = E_{01} - E_{0-1} = E^\circ(\mathrm{M}) + E^\circ(\mathrm{B_iH^+}) - E^\circ(\mathrm{MH^+}) - E^\circ(\mathrm{B_i})$$

On the other hand, the Gibbs free energy of reaction 1 at temperature T, $\Delta_i G^\circ_T$, appearing in eq 4 may be expressed as

$$\Delta_i G^\circ_T = \Delta_i E^\circ + \Delta_i H^\circ_{0\to T} - T\,\Delta_i S^\circ_T = \Delta_i E^\circ + \Delta_i G^\circ_{0\to T} \tag{9}$$

If we compare eq 4 and eq 8, the parameter a should be equal to 1.0, parameter b (i.e., the slope at half reaction efficiency) should be equated to $1/RT$, and parameter d (i.e., the shift of the thermokinetic curve on the energy axis) to the difference $\Delta_i G^\circ_T - \Delta_i E^\circ$, i.e., according to eq 9, to $\Delta_i G^\circ_{0\to T}$.

As evidenced in Table 3 the fitting parameter a is indeed close to unity, and plays simply a role of normalizing factor. The validity of the equalities $b = 1/RT$ and $d = \Delta_i G^\circ_{0\to T}$ as well as their consequences on the applicability of the thermokinetic methods will be now examined.

The Parameter b. A crucial question is that of the meaning of the temperature determined from the fitting parameter b. If, by analogy with the "kinetic" method, we call this quantity an apparent temperature $T_{\mathrm{app}} = 1/Rb$, its relationship with the temperature T of the thermalized reactants may be readily established.

It is first observed that, for the systems considered, the apparent temperature T_{app} closely follows the reactant temperature T. Accordingly, T_{app} is ranging from 328(±9) to 269(±9) K, from 526(±7) to 481(±5), and from 1019(±4) to 996(±4) K for temperatures $T = 298$, 500, and 1000 K, respectively. The absolute difference between the two temperatures T and T_{app} is thus lower than 30 K. A second observation is that, for a given T value, a slight decrease in T_{app} is systematically noted when passing from model I or IV, where reactant and products are structurally identical, to models involving more constrained $\mathrm{MH^+}$.

To understand the meaning of the apparent temperature T_{app} and its observed evolution, it should be emphasized that the ratio of rate constants k_{-1}/k_1 which intervene in the reaction efficiency RE (eq 2) is only dependent upon the sum of states of the two transition structures (see Figure 1). Since T_{app} is calculated from the slope b of the RE curve at RE = 0.5, it corresponds to $\sum P_{-1}^{\ddagger}(\Delta E^*_T)/\sum P_1^{\ddagger}(\Delta E'^*_{T'}) = 1$ and thus to hypothetical products with an excess energy $\Delta E'^*_{T'}$ giving the same sum of states as the reactants with an excess energy ΔE^*_T. For models II, III, V, VI, and VII, the sum of states $\sum P_{-1}^{\ddagger}(\Delta E)$ is lower than $\sum P_1^{\ddagger}(\Delta E)$ at any given energy ΔE. Thus, in order to attain the equality $\sum P_{-1}^{\ddagger}(\Delta E^*_T) = \sum P_1^{\ddagger}(\Delta E'^*_{T'})$, the critical energy of the hypothetical reaction should be increased in order to reduce $\sum P_1^{\ddagger}(\Delta E'^*_{T'})$. Consequently, for these models, $\Delta E'^*_{T'}$ is lower than ΔE^*_T and the temperature of the products, T', is lower than the temperature of the reactants, T. The apparent temperature T_{app} necessarily includes this phenomenon which is probably at the origin of the slight effect of the structure of the model on T_{app}. As a corollary, it may be also concluded that the critical energy E_{0-1}, which participates in the total internal energy E^* of the reaction intermediate $\mathrm{MHB_i^+}$, is not expected to influence the T_{app} values since only ΔE^*_T and $\Delta E'^*_{T'}$ have an incidence on the ratio of rate constants k_{-1}/k_1 which intervene in the reaction efficiency RE. We indeed control that identical results are obtained by changing E_{0-1} in the simulation. This situation is quite different from that encountered in the kinetic method[4] since, in the latter, the excess energy of the adducts $\mathrm{MHB_i^+}$ is a function of the observation time and consequently of the individual rate values which, in turn, are dependent on the critical energies.

The Parameter d. As indicated above, parameter d is expected to represent the thermodynamic quantity $\Delta_i G^\circ_{0\to T}$. This latter may be detailed into enthalpic and entropic contributions:

$$\Delta_i G^\circ_{0\to T} = \Delta_i H^\circ_{0\to T} - T\Delta_i S^\circ_T \tag{10}$$

thus leading to

$$\Delta_i G^\circ_T = \Delta_i E^\circ + \Delta_i H^\circ_{0\to T} - T\Delta_i S^\circ_T \tag{11}$$

The enthalpic and entropic terms appearing in eq 10 may be calculated by means of the usual formulas of statistical thermodynamic. It is evident that for models I and IV, since reactant and products are identical, $\Delta_i H^\circ_{0\to T}$, $\Delta_i S^\circ_T$, and consequently $\Delta_i G^\circ_{0\to T}$ are always equal to zero. The results obtained for the other models, II, III, V, VI, and VII, at the three selected temperatures $T = 298$, 500, and 1000 K are summarized in Table 4. Note that, using a more conventional entropy unit, models II, III, V, VI, and VII correspond to reactions (1) associated with a $\Delta_i S^\circ_{298}$ ranging between 10 and 40 J mol^{-1} K^{-1}.

Qualitatively, when $\Delta_i S^\circ_T$ is positive, eq 10 predicts that $\Delta_i G^\circ_{0\to T}$ would decrease with temperature T. Consideration of the values reported in Table 4 quantitatively confirms this expectation. Gibbs free energy terms $\Delta_i G^\circ_{0\to T}$ in the range ∼−30 to ∼−350 meV (3 to 35 kJ mol^{-1}) are calculated for models II, III, V, VI, and VII. The most striking observation concerns the comparison between the thermochemical quantity $\Delta_i G^\circ_{0\to T}$ and the fitting parameter d. Indeed, the matching between the two sets of values (Tables 3 and 4) is excellent even if, systematically, the absolute value of d is larger than that of $\Delta_i G^\circ_{0\to T}$. This shift is, however, lower than 8 meV (0.8 kJ mol^{-1}). Another means to visualize this observation is to consider, for a given temperature T, the RE vs $\Delta_i G^\circ_T$ curves of the model reactions merged on the same graph. This is shown in Figure 5 for $T = 298$ K; clearly, to a good approximation, all the curves cross the RE = 0.5 line at $\Delta_i G^\circ_T = 0$, whatever the model is, i.e., whatever the entropy term $\Delta_i S^\circ_T$ may be.

To summarize at this stage, the two main results established here are that, even for situations where $\Delta_i S^\circ_T$ is positive: (i) the apparent temperature $T_{\mathrm{app}} = 1/Rb$, resulting from the fitting procedure, corresponds closely to the true temperature of the thermalized reactants; (ii) the thermokinetic method provides, to an excellent approximation, the Gibbs free energy terms $\Delta_i G^\circ_T = \Delta_i E^\circ + \Delta_i G^\circ_{0\to T}$ at RE = 0.5.

The last point now remains to relate the term $\Delta_i G^\circ_T$ to the classical 298 K thermochemical quantities.

Obtaining Gas Phase Basicity and Proton Affinity by the Thermokinetic Method. The determination of gas phase basicity GB(M) or proton affinity PA(M) of the molecule of interest needs to express differently the quantity $\Delta_i G^\circ_T$. For reaction 1 at a temperature T, the Gibbs free energy $\Delta_i G^\circ_T$ is equal to

$$\Delta_i G^\circ_T = \Delta_i H^\circ_{298} + \Delta_i H^\circ_{298\to T} - T\Delta_i S^\circ_{298} - T\Delta_i S^\circ_{298\to T}$$

or, by introducing the 298 K gas phase basicities in order to apply the fitting function given by eq 5,

$$\Delta_i G^\circ_T = \mathrm{GB}_{298}(\mathrm{M}) - \mathrm{GB}_{298}(\mathrm{B_i}) - (T - 298)\Delta_i S^\circ_{298} + \Delta_i H^\circ_{298\to T} - T\Delta_i S^\circ_{298\to T} \tag{12}$$

TABLE 4: Thermochemical Data Relevant to the Relationship between $\Delta_iG°_T$ and $\Delta_iE°$ (in meV)

model	T	$\Delta_iH°_{0\to T}$	$T\Delta_iS°_T$	$\Delta_iG°_{0\to T}{}^a$	$\Delta_iH°_{298\to T}$	$T\Delta_iS°_{298\to T}$	$\Delta_iG°_{298\to T}{}^b$
II	298	18.0	51.9	−33.9	0	0	0
	500	21.6	91.8	−70.3	3.6	4.7	−1.1
	1000	24.4	187.9	−163.5	6.4	12.4	−6.0
III	298	34.1	104.1	−70.0	0	0	0
	500	41.0	183.8	−142.9	6.9	9.3	−2.4
	1000	46.4	375.8	−329.4	12.3	26.9	−14.6
V	298	6.3	35.1	−28.7	0	0	0
	500	6.8	59.4	−52.5	0.5	0.5	0
	1000	7.2	119.3	−112.1	0.9	1.6	−0.7
VI	298	18.0	67.9	−49.8	0	0	0
	500	20.6	117.4	−96.8	2.6	3.5	−0.9
	1000	22.7	237.9	−215.2	4.7	10.2	−5.5
VII	298	41.5	103.4	−61.9	0	0	0
	500	68.2	208.6	−140.4	26.7	35.1	−8.4
	1000	97.4	460.5	−363.1	55.9	113.6	−57.7

[a] $\Delta_iG°_{0\to T} = \Delta_iH°_{0\to T} - T\Delta_iS°_T$. [b] $\Delta_iG°_{298\to T} = \Delta_iH°_{298\to T} - T\Delta_iS°_{298\to T}$.

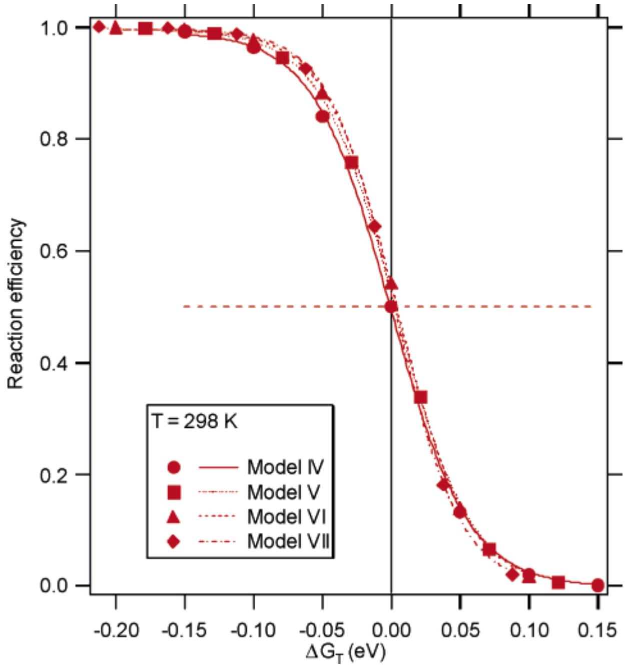

Figure 5. Thermokinetic plot as a function of the Gibbs free energy change for the reaction $MH^+ + B_i \to M + B_iH^+$ assumed to proceed at 298 K reactant temperature, with entropy change $\Delta_iS°_{298}$ ranging from 0 to 34 J mol^{-1} K^{-1} (models IV, V, VI, VII).

Thus, comparing eqs 12 and 5, the parameter c appearing in the latter should be equated to

$$c = GB_{298}(M) - (T - 298)\Delta_iS°_{298} + \Delta_iH°_{298\to T} - T\Delta_iS°_{298\to T} \quad (13)$$

In other words, when fitting the experimental RE vs $GB_{298}(B_i)$ points by eq 5, the RE = 0.5 value corresponds to the parameter c, i.e., to $GB_{298}(M)$ plus a correction term $\Delta G°_a = -(T - 298)\Delta_iS°_{298} + \Delta_iH°_{298\to T} - T\Delta_iS°_{298\to T}$.

Similarly, considering RE vs $PA_{298}(B_i)$ and fitting the data by a function

$$RE = a/[1 + \exp(b(c' - PA_{298}(B_i))] \quad (5')$$

the RE = 0.5 value will correspond to a parameter c' equal to

$$c' = PA_{298}(M) - T\Delta_iS°_{298} + \Delta_iH°_{298\to T} - T\Delta_iS°_{298\to T} \quad (13')$$

This may be easily shown by writing

$$\Delta_iG°_T = PA_{298}(M) - PA_{298}(B_i) + \Delta_iH°_{298\to T} - T\Delta_iS°_{298} - T\Delta_iS°_{298\to T} \quad (12')$$

In the preceding expressions, $\Delta_iS°_{298}$ is the 298 K entropy change of reaction 1, $\Delta_iS°_{298} = S_{298}°(M) + S_{298}°(B_iH^+) - S_{298}°(MH^+) - S_{298}°(B_i)$, and the terms $\Delta H°_{298\to T}$ and $\Delta S°_{298\to T}$ are the thermal corrections for enthalpy and entropy, respectively. Evaluation of the two latter quantities involves integration of the difference in molar heat capacities at constant pressure $\Delta C_p = C_p(M) + C_p(B_iH^+) - C_p(MH^+) - C_p(B_i)$ which, because of the structural similarities of $MH^+ + B_i$ on one hand and $M + B_iH^+$ on the other, is often assumed to essentially cancel to zero. In such circumstances, eqs 13 and 13′ may be approximated by

$$c \sim GB_{298}(M) - (T - 298)\Delta_iS°_{298} \quad (14)$$

$$c' \sim PA_{298}(M) - T\Delta_iS°_{298} \quad (14')$$

It should be emphasized that the neglect of the thermal corrections $\Delta H°_{298\to T}$ and $\Delta S°_{298\to T}$ is valid only in a limited temperature range and for systems not associated with a large entropy change. This may be illustrated by the thermochemical data quoted in Table 4 where the exact evaluation of the quantities $\Delta_iH°_{298\to T}$ and $T\Delta_iS°_{298\to T}$ for the models considered is reported. It appears that the entropic contribution $T\Delta_iS°_{298\to T}$ is always larger than $\Delta_iH°_{298\to T}$; as a consequence the total correction $\Delta_iG°_{298\to T} = \Delta_iH°_{298\to T} - T\Delta_iS°_{298\to T}$ is always negative. This latter attains, in the worst cases studied here (models III and VII, respectively), values of −2 and −8 meV at 500 K and −14 and −58 meV at 1000 K. This means that the error introduced by neglecting the sum $\Delta_iH°_{298\to T} - T\Delta_iS°_{298\to T}$ may be indeed negligible at 500 K but probably not at 1000 K since it may attain values of several kJ mol^{-1}.

Even if the approximation $\Delta_iH°_{298\to T} - T\Delta_iS°_{298\to T} \sim 0$ may be applied, eqs 14 and 14′ show that $\Delta_iS°_{298}$ may play a significant role in the determination of the thermochemical quantities $PA_{298}(M)$ and $GB_{298}(M)$ by the thermokinetic method. Two situations should be distinguished depending upon the importance of the $\Delta_iS°_{298}$ term.

Ideally, if reactants and products are structurally identical, $\Delta_iS°_{298} = 0$ and $\Delta_iG°_T$ and $\Delta_iH°_T$ are equal to $\Delta_iE°$ at any temperature T. It is thus expected that RE plots as a function of $GB_{298}(B_i)$ or $PA_{298}(B_i)$ would lead to $GB_{298}(M)$ and $PA_{298}(M)$ when RE takes the value 0.5. In practical situations, however,

$\Delta_i S°_{298}$ is not strictly zero and ΔE^*_T not strictly identical for each couple of molecules M and B_i. Moreover, the uncertainty on the experimental reaction efficiencies RE and on the tabulated $GB_{298}(B_i)$ or $PA_{298}(B_i)$[10] should be also considered. Experimentally, in the original study[3] involving several sets of monofunctional bases B_i, an empirical correction ΔG_a has been found necessary to correct the slightly overestimated $GB_{298}(M)$ values obtained by the thermokinetic method. In fact, the origin of this systematic shift, close to RT, is related to the mean value of the $\Delta_i S°_{298}$ terms which was not strictly zero but situated around 5−10 J mol^{-1} K^{-1} thus leading to a corrective ΔG_a term of ca. 5 kJ mol^{-1}.[3]

When the entropy of reaction 1, $\Delta_i S°_{298}$, is not negligible, it readily appears that the thermokinetic method, since typically operated at only one temperature, should be used carefully. According to eq 14, if the temperature of the reactant is close to 298 K, a plot of the reaction efficiency RE as a function of $GB_{298}(B_i)$ may allow the determination of $GB_{298}(M)$. By contrast, however, a plot of the reaction efficiency as a function of $PA_{298}(B_i)$ would lead only to the difference $PA_{298}(M) - T\Delta_i S°_{298}$, not to the pure 298 K proton affinity of the molecule of interest (eq 14′).

Toward an Extended Thermokinetic Method? Obviously, the problems encountered in the determination of the protonation thermochemistry by the thermokinetic method when the proton transfer reaction is associated with a significant entropy change may be overcome by several series of experiments conducted at several temperatures T. This may be done, for example, by using a suitable activation process or thermally controlled relaxation of the reactants. This situation is clearly reminiscent of that encountered with the kinetic method and its “extended” form.[4,11−14] Consequently, a similar procedure may thus be applied such as for example the use of $\ln[(1 - \mathrm{RE})/\mathrm{RE}]$ which, according to eq 4, is equal to $\Delta_i G°_T/RT$ and thus should be a linear function of the suitable energetic quantity (e.g., $\Delta_i E°$, $GB_{298}(B_i)$, or $PA_{298}(B_i)$).

Conclusions

The present study underlines the compatibility of the canonical and microcanonical formulations of the thermokinetic method when an orbiting transition state model is used in the rate constant calculation. It is demonstrated that the Gibbs free energy variation $\Delta_i G°_T$ of the proton transfer reaction $MH^+ + B_i \rightarrow M + B_iH^+$ corresponds to the reaction efficiency value of 0.5 at an apparent temperature T_{app}. The modeling also shows that this latter reproduces reasonably well the actual temperature T of the reactants. Consequently, in principle, the thermokinetic method may provide accurate 298 K gas phase basicity $GB_{298}(M)$, even if the entropy variation of the proton transfer reaction is not negligible. The related enthalpic term, proton affinity PA(M), may be obtained from a plot of the reaction efficiency vs $PA(B_i)$ only if the entropy variation is close to zero. To derive proton affinity and protonation entropy of polydentate molecules, the use of the thermokinetic method at several excitation energies appears necessary.

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