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Thermochemical Determinations by the Kinetic Method with Direct Entropy Correction[†]

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The kinetic method, which is based on the competitive dissociations of mass-selected cluster ions, has been increasingly applied in thermochemical determination mainly due to its simplicity and sensitivity. Its use, however, is limited by the requirement that the reference and unknown compounds be similar in structure. To address this limitation, entropic contributions are considered explicitly here. This allows the method to be applied in cases where neither the assumption of zero protonation entropy difference of the standard form nor the precondition of constant protonation entropy difference of the extended version of the method is satisfied. The validity of the proposed procedure for entropy correction is examined using urea as the test compound, and amides, ketones, ethylene glycol dimethyl ether, and polyols as the reference bases. After—but not before—appropriate entropy correction, the results show a linear correlation of the logarithm of the branching ratio versus proton affinity. Using data obtained as a function of collision energy, a second plot of the intercepts versus the slopes of the initial graph yields a value for the urea proton affinity (PA) of 868.4 ± 2.5 kJ/mol, a gas-phase basicity (GB) of 838.7 ± 3.0 kJ/mol, and a protonation entropy (ΔS_p) of 9.4 ± 0.5 J/mol·K. Experiments using different functionalized reference bases give similar results. The reported procedure extends the capabilities of the kinetic method in making thermochemical measurements and can be applied to the measurement of reaction entropies, provided enthalpies are known.

Introduction

Gas phase proton transfer (eq 1) is a reaction that has been studied quantitatively for more than 3 decades.[1−3] Many accurate thermochemical properties are based upon either direct or indirect measurement of proton-transfer equilibrium constants[4] or by using bracketing experiments to follow ion/molecule proton-transfer reactivity.[5,6] Such measurements have been essential in securing an understanding of intrinsic structural effects on acidity and basicity of molecules,[7] as well as providing solvation energetics.[8]

$$AH^+ + B \rightarrow A + BH^+ \tag{1}$$

The proton affinity (PA) is defined as the negative of the enthalpy change (ΔH) associated with protonation,[9] eq 2.

$$M + H^+ \rightarrow MH^+ \qquad PA \equiv -\Delta H_{\text{reaction}} \tag{2}$$

The gas-phase basicity (GB) is the negative of the free energy change for the above reaction and the corresponding reaction entropy ΔS can be expressed in terms of absolute entropies of the species involved [$\Delta S = S(MH^+) - S(M) - S(H^+)$]. Since

$$\Delta G = \Delta H - T\Delta S \tag{3}$$

the gas-phase basicity (GB) can be expressed in terms of the proton affinity (PA) and the temperature (T) dependent entropy change as shown in eq 4.

$$GB = PA + T\Delta S \tag{4}$$

The kinetic method, developed more than 2 decades ago,[10,11] is an approximate, semiquantitative method of acquiring relative thermochemical information by examining the relative rates of competitive dissociations of a cluster ion that includes the compound of interest, a reference compound and the ion to which binding occurs.[12−14]

As in other mass spectrometric methods for making thermochemical measurements, such as high-pressure mass spectrometry[4] and ion/molecule bracketing,[5,6] the roots of the kinetic method lie in proton transfer. However, the species selected for examination in the kinetic method is the proton bound dimeric cluster ion instead of the protonated monomers used as starting reactants in other methods. Assuming no reverse activation energy and that only structurally similar compounds are involved, dissociation of the mass-selected dimeric ion, $B{-}H^+{-}B_i$, may give rise to two protonated species, BH^+ and B_iH^+, via the two possible competitive dissociation channels k and k_i, shown in eq 5.

$$BH^+ + B_i \xleftarrow{k} B{-}H^+{-}B_i \xrightarrow{k_i} B + B_iH^+ \tag{5}$$

In the above equation, k is generally referred to the rate constant for the formation of BH^+ with unknown gas-phase thermochemistry, i.e., proton affinity (PA), gas-phase basicity (GB), and reaction entropy (ΔS), while k_i represents the rate constant for one of a series of reference bases having known values of these thermochemical properties. Because the competitive dissociations occur from a common ion, the logarithm of the ratio of rate constants can be expressed using uni-

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molecular reaction theory as[15]

$$\ln((k_i/k)) = \ln[([B_iH^+]/[BH^+])] \approx \ln(Q_i^*/Q^*) + \frac{\Delta\epsilon_0}{RT_{\rm eff}} \quad (6)$$

where Q_i* and Q* refer to the partition functions of the transition states of the two dissociation channels. The term $T_{\rm eff}$, called the "effective temperature", in one view, represents the characteristic temperature of the activated complexes that undergo competitive fragmentation during the instrument time window.[16] (There is continued discussion of whether $T_{\rm eff}$ is best viewed as a kinetic[16] or a thermodynamic[17] property.) The term $\Delta\epsilon_0$ is the difference in critical energies for the two dissociation channels. With the assumption that there are no (or equal) reverse barriers, the difference in critical energies can be replaced by the difference in PAs

$$\ln((k_i/k)) = \ln(([B_iH^+]/[BH^+])) \approx \ln(Q_i^*/Q^*) + \frac{PA(B_i) - PA(B)}{RT_{\rm eff}} \quad (7)$$

Under the same simplifying assumption, the term $\ln(Q_i^*/Q^*)$ is equivalent to the difference in reaction entropy between the two dissociation channels.[12,13] Substitution of $\ln(Q_i^*/Q^*)$ by the term $\Delta(\Delta S)/R$ leads to eq 8,

$$\ln((k_i/k)) = \ln(([B_iH^+]/[BH^+])) \approx \frac{PA(B_i) - PA(B)}{RT_{\rm eff}} + \frac{\Delta(\Delta S)}{R} \quad (8)$$

in which $\Delta(\Delta S)$ is defined as the reaction entropy difference between the two fragmentation channels. The entropic term $\Delta(\Delta S)/R$ can be canceled under the second assumption if *only* structurally similar reference and unknown species are involved, and the cancellation leads to the standard version[14] of the kinetic method described in eq 9 or the equivalent expression in which PA is replaced by GB. Plotting $\ln(k_i/k)$ vs PA(B_i) results in a straight line with slope of $1/RT_{\rm eff}$ and intercept of $-PA(B)/RT_{\rm eff}$. The proton affinity of the unknown can be derived simply as the ratio of the negative value of the intercept to the slope.

$$\ln((k_i/k)) = \ln(([B_iH^+]/[BH^+])) \approx \frac{PA(B_i) - PA(B)}{RT_{\rm eff}} \quad (9)$$

The main advantages of the kinetic method are its high sensitivity, even toward such subtle differences in thermochemical values as those caused by isotopic substitution,[18,19] and the fact that it allows rapid measurement, performed using any tandem mass spectrometer. The kinetic method has seen use in ion structure determinations,[20−22] internal energy measurements,[23,24] and chiral analysis of biological compounds,[25−27] in addition to its major application in thermochemistry determinations.[28−31]

Despite this usefulness, the kinetic method is restricted by the requirement that the entropy changes be equal for the reaction channels involving each reference and the unknown in order to eliminate entropic effects on the relative rate constants. This limitation has drawn criticism.[32] Several approaches address this issue. For instance, Squires advocated a single reference variant of the kinetic method[33] in which the mass selected cluster ions are composed of a single reference compound and a series of structurally similar compounds with unknown thermochemical properties. Under this "fixed" or "single reference" form of the kinetic method, a series of structurally similar unknowns was selected to maintain similar (nonzero) entropy differences between the two dissociation channels in each of the dimer pairs across the whole series.[34]

A related advance was made by Fenselau and co-workers,[35] and later contributed to by Wesdemiotis and his group.[36] In their original attempt at applying the kinetic method to biomolecules such as peptides, Fenselau and co-workers realized that getting a series of reference bases with similar structure to the unknown's would be difficult. However, if the reference bases chosen are dissimilar in structure to the unknown peptides but remain structurally similar among themselves, the entropic term $\Delta(\Delta S)/R$ in eq 8, while not negligible, but will likely remain constant. Thus a plot of $\ln(k_i/k)$ versus PA(B_i) should still yield a straight line. Moreover, the slopes and intercepts of the linear regressions derived from a series of such plots provide values for the effective temperature $T_{\rm eff}$ and apparent gas-phase basicity ($GB^{\rm app}$(B)). These quantities are related through eq 10

$$\frac{GB^{\rm app}(B)}{RT_{\rm eff}} \approx \frac{PA(B)}{RT_{\rm eff}} - \frac{\Delta(\Delta S)}{R} \quad (10)$$

To extract the values of enthalpy (PA(B)) and reaction entropy difference ($\Delta(\Delta S)$), a second plot was constructed by plotting the negative of the intercepts versus the slopes obtained from a series of experiments performed at different collision energies (equivalent to $GB^{\rm app}(B)/RT_{\rm eff}$ versus $1/RT_{\rm eff}$ at several values of $T_{\rm eff}$). This so-called extended version of the kinetic method[35,36] not only recognizes the presence of entropy effects but also can be used to provide values for relative reaction entropies in cases where the reference bases possess dissimilar structures from the unknown but remain structurally similar among themselves.

A surprising feature of the extended kinetic method was that the regression coefficient (R^2) from the second plot (negative intercept versus slope) was unity in each case studied.[35−38] Such excellent linearity simply implies that the slope and intercept are not independent. A statistical procedure has been developed by Armentrout in order to remove the covariance between the slope and intercept.[39] Instead of directly plotting $\ln(k_i/k)$ versus PA(B_i), the average proton affinity of the reference bases [PA($B_i^{\rm avg}$)] is subtracted from the proton affinities of the unknown and reference bases in eq 8. The modified equation is rewritten explicitly in eq 11. A plot of $\ln(k_i/k)$ versus $\Delta PA(B_i)$, the difference in PAs of the reference bases and the average value of PA($B_i^{\rm avg}$), removes the covariance between the slope ($1/RT_{\rm eff}$) and the intercept $\{-[PA(B) - PA(B_i^{\rm avg})]/RT_{\rm eff} + \Delta(\Delta S)/R\}$ obtained from the initial plot.

$$\ln((k_i/k)) \approx \frac{PA(B_i) - PA(B_i^{\rm avg})}{RT_{\rm eff}} - \left[\frac{PA(B) - PA(B_i^{\rm avg})}{RT_{\rm eff}} - \frac{\Delta(\Delta S)}{R}\right] \quad (11)$$

More recently, a temperature corrected kinetic method (TCKM) has been proposed by using a triple plotting procedure to obtain improved relative thermochemical measurements.[40] The gas-phase basicity of the analyte GB^T(B), defined in eq 12, can be plotted against effective temperature $T_{\rm eff}$ for experiments done at various kinetic energies. This allows the direct determination of the reaction entropy ΔS(B) of the analyte rather than the difference $\Delta(\Delta S)$ between the reaction entropy of the analyte and the average value for a series of reference bases.

$$\mathrm{GB}^{T}(\mathrm{B}) = \mathrm{PA}(\mathrm{B}) + T_{\mathrm{eff}}\Delta S(\mathrm{B}) \quad (12)$$

This method gives excellent data although it has been criticized as incorrectly representing the errors through excessive averaging and using three plots where two should suffice.[41]

In the general case where structurally dissimilar reference bases are used, the reaction entropy difference $\Delta(\Delta S)$ will not be a constant and a plot of $\ln(k_i/k)$ vs $\mathrm{PA}(\mathrm{B_i})$ will not yield a straight line. This difficulty can be overcome simply by rearranging eq 8 and directly incorporating the individual entropic contributions $(\Delta S(\mathrm{B_i})/R)$ into the logarithm of the ratio of the relative rates of dissociation. The method presented here overcomes the limitations of the TCKM procedure and was arrived at independently by Armentrout.[42] Importantly, the entropy corrected kinetic method (ECKM) can be applied to structurally dissimilar reference bases. The relationship on which it is based is shown in eq 13.

$$\ln((k_i/k)) - (\Delta S(\mathrm{B_i})/R) \approx (\mathrm{PA}(\mathrm{B_i})/RT_{\mathrm{eff}}) - [(\mathrm{PA}(\mathrm{B})/RT_{\mathrm{eff}}) + (\Delta S(\mathrm{B})/R)] \quad (13)$$

Applying the definition of gas-phase basicity (GB) given in eq 4 and substituting T_{eff} for T, this simplifies to eq 14,

$$\ln((k_i/k)) - (\Delta S(\mathrm{B_i})/R) \approx (\mathrm{PA}(\mathrm{B_i})/RT_{\mathrm{eff}}) - (\mathrm{GB}(\mathrm{B})/RT_{\mathrm{eff}}) \quad (14)$$

Thus, a plot of the entropy corrected term $[\ln(k_i/k) - \Delta S(\mathrm{B_i})/R]$ vs $\mathrm{PA}(\mathrm{B_i})$ will yield a straight line with slope $1/RT_{\mathrm{eff}}$ and an intercept given by $-\mathrm{GB}(\mathrm{B})/RT_{\mathrm{eff}}$. By varying the collision energy, a second plot can be made by plotting the negative value of the intercept $\mathrm{GB}(\mathrm{B})/RT_{\mathrm{eff}}$ versus the slope $1/T_{\mathrm{eff}}$. This plot gives the gas-phase basicity of the analyte. A third plot of GB vs T_{eff} then yields the proton affinity and the reaction entropy $\Delta S(\mathrm{B})$. Note, however, the new requirement that protonation entropy values be available.

In this study, particular cases are presented to demonstrate that by introducing an entropy corrected branching ratio term, $\ln(k_i/k) - \Delta S(\mathrm{B_i})/R$, the kinetic method can be applied in cases where structurally dissimilar reference bases are used.

Experimental Procedures

A triple quadrupole mass spectrometer (TSQ 700, ThermoFinnigan, San Jose, CA) was employed to conduct all experiments, with the ion source and manifold temperatures maintained at 150 and 70°C, respectively. Volatile liquid samples were allowed to leak into the ion source through a modified GC inlet via a Granville Philips leak valve (Granville Phillips Co., Boulder, CO) while the solid urea was introduced by depositing a 1 μL solution in methanol onto the rhenium wire filament of a direct evaporation probe. The temperature of the direct evaporation probe was first raised from ambient to 300 °C in 1 min, then kept constant at this temperature for 2 min during which time data were acquired before finally being increased to 800 °C in 1 min to pyrolyze any remaining material. The ions of interest were mass selected in the first quadrupole Q1 and activated by collision in the second quadrupole Q2 using argon at a nominal pressure below 0.2 mTorr to maintain single collision conditions. The dissociation products were mass analyzed by scanning the third quadrupole Q3 of the triple quadrupole. Experimental data were collected at several different collision energies. Each peak ratio measurement was made in triplicate with each measurement made by averaging 50 scans.

All compounds were commercially available (Aldrich Chemical Co., Milwaukee, WI) and used without further purification. The Thomson unit (1 Th = 1 atomic mass per unit positive charge) is employed to describe mass/charge ratios (m/z).[43]

Results and Discussion

To check the validity of the proposed entropy corrected kinetic method, a compound having known thermochemical properties is needed. This compound will be treated as the test compound having unknown thermochemical properties during examination of the entropy corrected kinetic method. Neglecting entropic contributions, the proton affinity and gas phase basicity of urea have been determined recently by the standard version of the kinetic method using a series of chemically similar compounds as references.[44,45] In the present study, dissimilar compounds are employed as references and urea is treated as the test compound to examine the validity of the proposed entropy corrected version of the kinetic method.

Entropy Terms and Their Relationships. Prior to the discussion of results of the entropy corrected version of the method, it is desirable to first address the issue of selecting appropriate entropy values for the two competitive reactions involved. It is important to recognize that the dimeric cluster ion in eq 5 examined by the kinetic method is in fact an activated species and that the measured ion abundance ratio is controlled by $\Delta(\Delta S^{\neq})$, the difference in activation entropies of the two competing reactions.[37] Relying upon the fact that for each reaction channel, the transition state sufficiently closely resembles the products, we may make the approximations $\Delta S_i(\mathrm{prod}) \approx \Delta S_i{}^*(\mathrm{trans})$, $\Delta S(\mathrm{prod}) \approx \Delta S^*(\mathrm{trans})$, which leads to $\Delta S_i(\mathrm{prod}) - \Delta S(\mathrm{prod}) \approx \Delta S_i{}^*(\mathrm{trans}) - \Delta S^*(\mathrm{trans})$. This is equivalent to $\Delta(\Delta S)(\mathrm{prod}) \approx \Delta(\Delta S^*)(\mathrm{trans})$. The above approximation can be made for each reaction channel if this channel has no (or a very small) reverse activation barrier, as pointed out earlier. For the loosely bound complexes of interest, $\Delta(\Delta S^{\neq})$ is thus assumed to be very similar to the corresponding reaction entropy difference $(\Delta(\Delta S))$.[15] As a result, the more accessible relative reaction entropies can be used instead of $\Delta(\Delta S^{\neq})$.

Direct incorporation of the contribution from the reaction entropy difference and correction of the logarithm of the ratio of the relative rates of dissociation by the ratio of protonation entropy and the gas constant R ($R = 8.31$ J/mol·K), as shown earlier in eq 13, should be a valid procedure. In practice, since the reaction entropy $[\Delta S(\mathrm{B_i})]$ includes a constant value, the absolute entropy of the proton ($S(\mathrm{H^+})$), the absolute value of $\Delta S(\mathrm{B_i})/R$ is generally much larger than that of $\ln(k_i/k)$, i.e., $|\Delta S(\mathrm{B_i})/R| \gg |\ln(k_i/k)|$. It is therefore convenient to express the entropy change upon protonation using the protonation entropy, ΔS_p $[\Delta S_p = S(\mathrm{MH^+}) - S(\mathrm{M})]$.[9]

In any event, since the entropy of the proton ($S(\mathrm{H^+}) = 108.9$ J/mol·K) cancels in eq 13, the reaction entropy difference $\Delta(\Delta S)$ can be substituted by the difference of the two protonation entropies $\Delta(\Delta S_p)$ using values obtained directly from the literature.[9] Excluding the absolute entropy of the proton, the absolute values of the entropy of protonation over the gas constant $\Delta S_p(\mathrm{B_i})/R$ are generally much smaller than those of $\ln(k_i/k)$, i.e., $|\Delta S_p(\mathrm{B_i})/R| \ll |\ln(k_i/k)|$. Thus, the correction of $\ln(k_i/k)$ made using protonation entropies should better represent the actual entropy change between the two competing reaction channels. When using the entropy of protonation ΔS_p, the kinetic method takes the form

$$\ln((k_i/k)) - (\Delta S_p(\mathrm{B_i})/R) \approx (\mathrm{PA}(\mathrm{B_i})/RT_{\mathrm{eff}}) - [(\mathrm{PA}(\mathrm{B})/RT_{\mathrm{eff}}) + (\Delta S_p(B)/R)] \quad (15)$$

TABLE 1: Thermochemical Values for Reference Compounds

reference compounds		PA (kJ/mol)[a]	GB (J/mol)[a]	ΔS_p (J/mol·K)
series I	*N*-methyl acetamide	888.5	857.6	5.0
	acetophenone	861.1	829.3	2.0
	N,*N*-dimethylformamide	887.5	856.6	5.0
	ethylene glycol dimethyl ether	858.0	820.2	−18.0
series IIA	*N*-methyl acetamide	888.5	857.6	5.0
	acetophenone	861.1	829.3	2.0
	N,*N*-dimethylformamide	887.5	856.6	5.0
	dimethyl sulfoxide	884.4	853.7	5.8
	thiourea	893.7	863.9	9.0
series IIB	glycerol	874.8	820.0	−75.0
	cis-1,2-cyclopentanediol	885.6	853.1	0.0
	1,2,4-butanetriol	905.9	841.0	−109.0
	1,4-butanediol	915.6	854.9	−95.0

[a] PA, GB, and ΔS_p values taken from literature.[9]

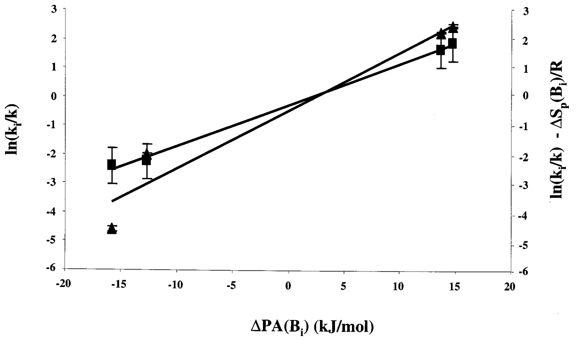

Figure 1. Kinetic method plots for urea using series I as test reference bases at collision energy 10 eV. The uncertainties shown on the *y*-axis are one standard deviation. (▲) Standard method plot: $\ln(k_i/k)$ versus $\Delta PA(B_i)$; regression coefficient (R^2) = 0.9458. (■) Entropy corrected method plot, $\ln(k_i/k) - \Delta S_p(B_i)/R$ versus $\Delta PA(B_i)$: Regression coefficient (R^2) = 0.9972. Uncertainties of ±5 J/mol.K in $\Delta S_p(B_i)$ and uncertainties of ±5 kJ/mol in $\Delta PA(B_i)$ are included for each reference base.

Application of the Entropy Corrected Kinetic Method. The objective of this section is to test the concept just noted, viz., that if the protonation entropies of the reference bases are known, then these values can be directly substituted into eq 15 to make entropy-corrected thermochemical measurements. Consider for instance, a set of four reference bases: *N*-methyl acetamide, acetophenone, *N*,*N*-dimethylformamide, and ethylene glycol dimethyl ether termed series I. The proton affinities PA, gas-phase basicities GB, and the entropies of protonation ΔS_p of the above species are listed in Table 1. In this study, *N*-methyl acetamide, acetophenone, and *N*,*N*-dimethylformamide are regarded as structurally similar reference bases when compared with urea since protonation of the above species is expected to occur at the nonbonding electrons of oxygen, analogously to the protonation of urea and its analogs.[46] On the other hand, ethylene glycol dimethyl ether is a well-known bidentate complexing agent for inorganic and organic cations. Formation of intramolecular hydrogen bonding upon protonation of the ether creates constrained structures. As a result, significant entropy loss occurs upon the protonation of ethylene glycol dimethyl ether.[47,48]

When using the above four compounds as reference bases and plotting the logarithms of the branching ratio $\ln(k_i/k)$ versus the proton affinity difference $\Delta PA(B_i)$, typical data for collision energy 10 eV are shown in Figure 1. In this plot, the average proton affinity $PA(B_i^{avg})$ is taken as the mean PA value of the above four reference bases in series I [$PA(B_i^{avg})$ = 873.8 kJ/mol]. From Figure 1, it is clear that, in the initial plot without entropy correction, one point deviates substantially from the straight line. However, a much smaller deviation in this point is observed when the $\ln(k_i/k)$ value for each reference base is corrected by the entropy contribution. The substantial deviation observed in the initial plot is due to the limitation of the kinetic method which requires either zero or a constant difference in relative reaction entropies. Similar behavior was also observed at other collision energies from 1 to 20 eV with the data being listed in Table 2.

The entropy corrected kinetic method allows one to overcome one of the limitations of the kinetic method, which limits the choice of reference bases to those that represents a family of structurally similar compounds. By directly incorporating the entropic term ($\Delta S_p(B_i)/R$) into the logarithm of the branching ratio, an entropy corrected logarithm of the branching ratio term $\ln(k_i/k) - \Delta S_p(B_i)/R$ is obtained. To remove the correlation suggested earlier, we adopt Armentrout's improved double plotting method[39] and eq 13 is modified as follows:

$$\ln((k_i/k)) - (\Delta S_p(B_i)/R) \approx \frac{PA(B_i) - PA(B_i^{avg})}{RT_{eff}} - \left[\frac{PA(B) - PA(B_i^{avg})}{RT_{eff}} + (\Delta S_p(B)/R)\right] \quad (16)$$

The average proton affinity $PA(B_i^{avg})$ is identical to that used in the standard method plot. When plotting the entropy corrected term $\ln(k_i/k) - \Delta S_p(B_i)/R$ versus $\Delta PA(B_i^{avg})$, smaller deviations were observed in comparison with the corresponding initial plot without entropy correction. However, significantly higher uncertainties were observed with the entropy corrected data in comparison with the original data due to the incorporation of higher uncertainties from the literature values (±5 J/mol·K in ΔS_p). Comparison of the two plots before and after entropy correction at collision energy of 10 eV, is illustrated in Figure 1. The effective temperature can be extrapolated from the slope $1/RT_{eff}$ given by the plot based on eq 16, and the intercept which is given by

$$-\left[\frac{PA(B) - PA(B_i^{avg})}{RT_{eff}} + (\Delta S_p(B)/R)\right]$$

The weighted intercept and slope derived from the initial plot are −0.302 ± 0.075 and 0.141 ± 0.005, respectively. After the entropy correction, acetophenone and ethylene glycol dimethyl ether lie in opposite sides relative of the resulting line, which suggests a significant entropy contribution in the case of ethylene glycol dimethyl ether. Similar results obtained at other collision energies between 1 and 20 eV are listed in Table 3.

According to eq 16, a further plot of the negative value of the intercept

$$\frac{PA(B) - PA(B_i^{avg})}{RT_{eff}} + (\Delta S_p(B)/R)$$

versus the slope $1/RT_{eff}$ should yield a second straight line with a slope given by the proton affinity difference $PA(B) - PA(B_i^{avg})$ and an intercept given by the protonation entropy term $\Delta S_p(B)/R$. It is important to point out that the entropy corrected method directly gives the entropy term instead of the entropy difference. The entropy of protonation $\Delta S_p(B)$ can be converted to the reaction entropy (ΔS) simply by subtracting this value from the absolute entropy of the proton ($S(H^+)$). With the results from as many as twenty different collision energies (Table 4),

TABLE 2: Experimental Data[a] for Series I Reference Bases

	$\ln(k_i/k)$[b]			
collision energies (eV)	*N*-methyl acetamide	ethylene glycol dimethyl ether	*N*,*N*-dimethylformamide	acetophenone
1	4.26 ± 0.08	−5.63 ± 0.18	3.35 ± 0.12	−2.76 ± 0.06
2	4.17 ± 0.06	−5.77 ± 0.12	3.59 ± 0.09	−2.77 ± 0.12
3	3.78 ± 0.11	−5.16 ± 0.20	2.64 ± 0.06	−2.51 ± 0.08
4	3.59 ± 0.12	−5.15 ± 0.09	3.42 ± 0.15	−2.44 ± 0.04
5	3.54 ± 0.02	−5.30 ± 0.14	3.14 ± 0.14	−2.35 ± 0.02
6	3.41 ± 0.09	−5.01 ± 0.12	2.91 ± 0.02	−2.23 ± 0.05
7	3.30 ± 0.04	−5.11 ± 0.02	2.65 ± 0.01	−2.54 ± 0.10
8	3.01 ± 0.08	−5.10 ± 0.16	2.54 ± 0.07	−2.30 ± 0.09
9	2.89 ± 0.07	−4.89 ± 0.06	2.34 ± 0.05	−2.13 ± 0.02
10	2.44 ± 0.06	−4.57 ± 0.08	2.21 ± 0.03	−2.01 ± 0.04
11	2.49 ± 0.04	−4.66 ± 0.12	2.14 ± 0.12	−1.86 ± 0.05
12	2.34 ± 0.10	−4.78 ± 0.11	2.11 ± 0.02	−1.83 ± 0.08
13	2.21 ± 0.02	−4.74 ± 0.18	2.21 ± 0.01	−1.75 ± 0.14
14	2.10 ± 0.05	−4.63 ± 0.20	1.93 ± 0.05	−1.87 ± 0.04
15	2.00 ± 0.08	−4.54 ± 0.04	1.38 ± 0.06	−1.92 ± 0.02
16	1.92 ± 0.06	−4.45 0.09	1.76 ± 0.04	−1.86 ± 0.05
17	1.85 ± 0.03	−4.71 ± 0.02	1.24 ± 0.02	−1.74 ± 0.02
18	1.79 ± 0.02	−4.40 ± 0.13	1.17 ± 0.02	−1.56 ± 0.07
19	1.72 ± 0.02	−4.59 ± 0.10	1.14 ± 0.03	−1.70 ± 0.05
20	1.67 ± 0.04	−4.71 ± 0.08	1.34 ± 0.05	−1.32 ± 0.02

[a] Values given as the average of triplicate measurements. [b] Values given as the average value ± standard deviation.

TABLE 3: Entropy Corrected Data[a] for Series I Reference Bases

	$\ln(k_i/k) - \Delta S_p(B_i)/R$[b]			
collision energies (eV)	*N*-methyl acetamide	ethylene glycol dimethyl ether	*N*,*N*-dimethylformamide	acetophenone
1	3.66 ± 0.61	−3.46 ± 0.63	2.75 ± 0.61	−3.00 ± 0.60
2	3.57 ± 0.60	−3.60 ± 0.61	2.99 ± 0.61	−3.01 ± 0.61
3	3.18 ± 0.61	−3.00 ± 0.63	2.04 ± 0.60	−2.75 ± 0.61
4	2.99 ± 0.61	−2.98 ± 0.61	2.82 ± 0.62	−2.68 ± 0.60
5	2.94 ± 0.60	−3.14 ± 0.62	2.54 ± 0.62	−2.59 ± 0.60
6	2.81 ± 0.61	−2.84 ± 0.61	2.31 ± 0.60	−2.47 ± 0.60
7	2.70 ± 0.60	−2.94 ± 0.60	2.05 ± 0.60	−2.78 ± 0.61
8	2.41 ± 0.61	−2.94 ± 0.62	1.94 ± 0.60	−2.54 ± 0.61
9	2.29 ± 0.60	−2.72 ± 0.60	1.74 ± 0.60	−2.37 ± 0.60
10	1.84 ± 0.60	−2.40 ± 0.61	1.61 ± 0.60	−2.25 ± 0.60
11	1.89 ± 0.60	−2.50 ± 0.61	1.54 ± 0.61	−2.10 ± 0.60
12	1.74 ± 0.61	−2.61 ± 0.61	1.51 ± 0.60	−2.07 ± 0.60
13	1.61 ± 0.60	−2.58 ± 0.63	1.61 ± 0.60	−1.99 ± 0.62
14	1.50 ± 0.60	−2.46 ± 0.63	1.33 ± 0.60	−2.11 ± 0.60
15	1.34 ± 0.61	−2.38 ± 0.60	0.78 ± 0.60	−2.16 ± 0.60
16	1.32 ± 0.60	−2.28 ± 0.61	1.16 ± 0.60	−2.10 ± 0.60
17	1.25 ± 0.60	−2.54 ± 0.60	0.64 ± 0.60	−1.98 ± 0.60
18	1.19 ± 0.60	−2.24 ± 0.61	0.57 ± 0.60	−1.80 ± 0.60
19	1.12 ± 0.60	−2.42 ± 0.61	0.54 ± 0.60	−1.90 ± 0.60
20	1.07 ± 0.60	−2.54 ± 0.61	0.74 ± 0.60	−1.56 ± 0.60

[a] Assuming the uncertainties in $\Delta S_p(B_i)$ are ± 5 J/mol.K. [b] Values given as derived value ± standard deviation.

the second plot using the negative values of the intercept versus the slopes obtained from the initial plot yields a proton affinity (PA) of urea of 868.4 ± 2.5 kJ/mol and a protonation entropy ΔS_p of 9.4 ± 0.5 J/mol.K with a linear regression coefficient $R^2 = 0.8877$. This plot is shown in Figure 2. The reaction entropy (ΔS) and gas-phase basicity (GB) for urea derived from the PA and ΔS_p are 99.5 ± 5.0 J/mol.K and 838.7 ± 3.0 kJ/mol, respectively. Since the uncertainties associated with the literature values (± 5 J/mol·K in ΔS_p) are significantly higher than the experimental uncertainties, it should be possible to minimize the uncertainties of the derived thermochemical values by sampling more collision energies. That this procedure is not entirely successful is evident from the shape of Figure 2: sampling fewer points in the same energy range or removing some points from either the beginning or the end of the plot results in slightly different thermochemical values.

The intercepts and slopes from the second plot as well as the derived thermochemical properties are listed in Table 5. The derived gas-phase proton affinity and basicity values are slightly lower than the reported experimental PA and GB values using the standard kinetic method.[44] ($PA_{lit} = 873.5$ kJ/mol, $GB_{lit} = 841.6$ kJ/mol)

Protonation Entropy Differences Derived from the Extended Kinetic Method. The aim of this section is to test whether it is also possible to apply the entropy corrected kinetic method when the protonation entropies are not directly available or when inconsistent values exist in the literature. This is done by determining a $\Delta(\Delta S)$ value using the extended kinetic method and using it instead of literature values in the ECKM. For example, consider a group of reference bases, Series II, made up of nine species that can be divided into two subseries, series IIA,B (Table 1). Series IIA includes five reference bases: *N*-methyl acetamide, acetophenone, *N*,*N*-dimethylformamide, dimethyl sulfoxide, and thiourea, while series IIB is comprised of four diols or polyols: glycerol, *cis*-1, 2-cyclopentanediol, 1, 2, 4-butanetriol, and 1, 4-butanediol. Within each subseries, the reference bases have similar structures. However, the protonation entropies vary significantly even within the same

TABLE 4: Weighted Intercepts and Slopes Obtained from the Initial Entropy Corrected Plot[a] for Series I as a Function of Collision Energy

collision energies (eV)	intercept[b]	slope[b]
1	−0.015 ± 0.181 (0.193)	0.226 ± 0.013 (0.013)
2	−0.014 ± 0.092 (0.099)	0.232 ± 0.006 (0.007)
3	−0.134 ± 0.253 (0.270)	0.193 ± 0.018 (0.019)
4	0.035 ± 0.080 (0.086)	0.201 ± 0.006 (0.006)
5	−0.062 ± 0.053 (0.057)	0.197 ± 0.004 (0.004)
6	−0.050 ± 0.093 (0.099)	0.183 ± 0.006 (0.007)
7	−0.244 ± 0.154 (0.165)	0.184 ± 0.011 (0.012)
8	−0.282 ± 0.082 (0.088)	0.173 ± 0.006 (0.006)
9	−0.267 ± 0.104 (0.111)	0.160 ± 0.007 (0.008)
10	−0.302 ± 0.075 (0.080)	0.141 ± 0.005 (0.006)
11	−0.292 ± 0.053 (0.057)	0.141 ± 0.004 (0.004)
12	−0.360 ± 0.036 (0.038)	0.140 ± 0.002 (0.003)
13	−0.337 ± 0.053 (0.056)	0.137 ± 0.004 (0.004)
14	−0.437 ± 0.016 (0.017)	0.130 ± 0.001 (0.001)
15	−0.590 ± 0.131 (0.140)	0.118 ± 0.009 (0.009)
16	−0.477 ± 0.048 (0.051)	0.120 ± 0.003 (0.004)
17	−0.660 ± 0.135 (0.144)	0.113 ± 0.009 (0.010)
18	−0.569 ± 0.133 (0.142)	0.102 ± 0.009 (0.010)
19	−0.677 ± 0.125 (0.133)	0.106 ± 0.009 (0.009)
20	−0.574 ± 0.174 (0.186)	0.105 ± 0.012 (0.013)

[a] $\ln(k_i/k) - \Delta S_p(B_i)/R$ versus $\Delta PA(B_i)$. [b] Values given as derived value ± standard deviation (90% confidence limits).

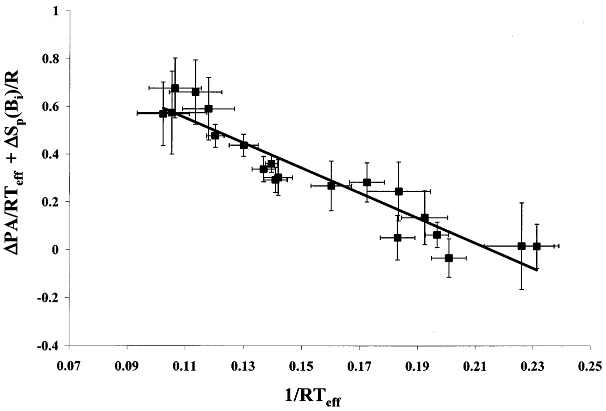

Figure 2. Double plot using the negative value of the intercept (weighted) versus the slope (weighted) obtained from the initial entropy corrected kinetic method plot of series I for the determination of the proton affinity and entropy of protonation of urea: plot of $[PA(B) - PA(B_i^{avg})]/RT_{eff} + (\Delta S_p(B)/R)$ versus $1/RT_{eff}$ using the effective temperature values obtained from twenty different collision energies ranging from 1 to 20 eV. The uncertainties shown on both the *x*-axis and the *y*-axis are one standard deviation. Regression coefficient (R^2) = 0.8877.

subseries. For instance, the four reference bases listed in series IIB are all diols or polyols and similar intramolecular hydrogen bonding is expected upon protonation. Their protonation entropies ΔS_p obtained directly from the literature, however, vary from 0 to −109 J/mol·K. As a result, direct incorporation of the above values into the logarithm of the branching ratio must give erroneous results.

Since each subseries meets the requirement of maintaining similar structures among the reference bases, it is possible to apply the extended version of the kinetic method to each subseries and obtain an averaged protonation entropy. A typical kinetic method plot is illustrated in Figure 3. In this plot, the average proton affinity $PA(B_i^{avg})$ is 883.0 kJ/mol for series IIA and 895.5 kJ/mol for series IIB. Using the same collision energy of 15 eV, a plot of $\ln(k_i/k)$ vs $\Delta PA(B_i)$ yields two almost parallel lines representing subseries IIA,B. On the basis of eq 11, the weighted intercept ($-GB^{app}(B)/RT_{eff}$) and slope ($1/RT_{eff}$) for series IIA, obtained from the initial plot, are 1.241 ± 0.164 and 0.145 ± 0.014, respectively. For series IIB, these values are −4.135 ± 0.104 and 0.148 ± 0.006, respectively. Similar parallel plots are also observed at collision energies 13, 14, 17, 18, and 19 eV (data are listed in the attached Supporting Information). A further plot of the negative of the intercept ($GB^{app}(B)/RT_{eff}$) versus the slope ($1/RT_{eff}$) over a series of collision energies yields the proton affinity (PA) and reaction entropy difference $\Delta(\Delta S)$. The urea proton affinity resulting from the double plot of series IIA is 869.2 ± 4.0 kJ/mol while series IIB yields the value 874.8 ± 3.2 kJ/mol. The reaction entropy differences resulting from the two plots are listed in Table 5.

The reaction entropy difference recorded for urea and series IIB is 60.4 ± 2.7 J/mol·K while the value for series IIA is much smaller (5.2 ± 3.7 J/mol·K) due to the structural similarity of series IIA with urea. Since the reaction entropy difference $\Delta(\Delta S)$ is identical to the protonation entropy difference $\Delta(\Delta S_p)$, it is possible to directly incorporate the protonation entropy difference between series IIA,B into $\ln(k_i/k)$ of series IIB, while $\ln(k_i/k)$ from series IIA need not be corrected. A plot of the entropy corrected ratio versus the proton affinity difference $\Delta PA(B_i)$, including all reference bases in series IIA,B, was therefore performed using the extended method data in this ECKM determination.

In this case, the average proton affinity ($PA(B_i^{avg})$ = 888.6 kJ/mol) is taken as the mean proton affinity of series IIA,B, including all nine reference bases. A typical figure showing the fitting of series IIA,B by plotting the entropy corrected ratio versus the proton affinity difference at collision energy 15 eV is illustrated in Figure 4. It is satisfying that this plot includes all nine reference bases with multiple compounds having dissimilar structures. From Figure 4, the weighted intercept (1.858 ± 0.130) and slope (0.139 ± 0.009) were obtained. Similar corrections at other collision energies were also performed. The double plotting method can be used on the entire data set to derive corrected thermochemical properties of urea, PA = 867.7 ± 2.3 kJ/mol, GB = 837.8 ± 2.8 kJ/mol, and ΔS_p = 8.4 ± 1.7 J/mol·K, as shown in Table 5.

It is important to point out that as the reaction entropy difference between the two competitive dissociation channels becomes larger, the results become less precise. For instance, the difference of 55 J/mol·K between series IIA,B makes it likely that one reaction possesses a reverse activation barrier. As a result, substitution of $\ln(Q_i^*/Q^*)$ by the $-\Delta(\Delta S)$ term in eq 7 becomes questionable. Furthermore, the above approximation becomes increasingly unreliable as the differences in measured $\Delta(\Delta S)$ values increases. Another issue not addressed is the use of T_{eff} instead of T in eq 15 and earlier equations. The effects of this assumed equality have not been explored. (Compare the curvature in Figure 2 and the data of Ervin.[49])

In summary, in the above attempts to address one limitation of the kinetic method, the protonation entropy of each reference compound is directly incorporated into the logarithm of the ratio of the relative abundance of two competitive dissociation channels in cases where the reference bases employed are dissimilar to the analyte. The procedure used in this new method includes a plot of this entropy corrected branching ratio versus the proton affinity which yields a straight line with slope and intercept given by $1/RT_{eff}$ and $-GB(B)/RT_{eff}$, respectively. A statistical approach (see Supporting Information) is adopted for proper linear regression analysis as well as to obtain the weighted intercepts and slopes. By varying collision energies, a second plot of the negative value of the intercept $[GB(B)/RT_{eff}]$ versus the slope ($1/T_{eff}$) is made and it yields the proton

TABLE 5: Proton Affinity, Gas-Phase Basicity, and Entropy of Protonation of Urea Derived from the Second Plot[a]

reference series	intercept	slope	PA (kJ/mol)	GB (kJ/mol)	ΔS_p (J/mol·K)	ΔS (J/mol·K)[b]	$\Delta(\Delta S)$ (J/mol·K)
series I	1.13 ± 0.07 (0.03)	−5.37 ± 0.46 (0.18)	868.4 ± 2.5 (2.5)[c]	838.7 ± 3.0 (2.9)[c]	9.4 ± 0.5 (0.2)[c]	99.5 ± 5.0 (5.0)[c]	*d*
series IIA	0.62 ± 0.45 (0.36)	−13.80 ± 3.30 (2.60)	869.2 ± 4.0 (3.4)[e]				5.2 ± 3.7 (3.0)[e]
series IIB	7.27 ± 0.32 (0.26)	−20.66 ± 2.07 (1.64)	874.8 ± 3.2 (3.0)[e]				60.4 ± 2.7 (2.1)[e]
series IIA,B	1.01 ± 0.21 (0.16)	−20.86 ± 1.52 (1.20)	867.7 ± 2.3 (2.1)[c]	837.8 ± 2.8 (2.6)[c]	8.4 ± 1.7 (1.4)[c]	100.5 ± 5.3 (5.2)[c]	

[a] Values given as derived value ± standard deviation (90% confidence limits). [b] Calculated as ΔS (J/mol·K) = 108.9 − ΔS_p. [c] From the entropy corrected kinetic method. [d] Not applicable. [e] From the extended kinetic method.

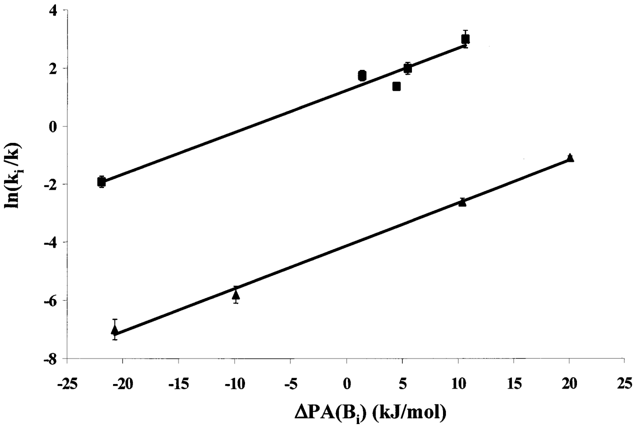

Figure 3. Kinetic method plots, $\ln(k_i/k)$ versus $\Delta PA(B_i)$ for reference bases in series IIA,B using urea as the test compound at collision energy 15 eV. The uncertainties shown on the *y*-axis are one standard deviation. (■) Series IIA: regression coefficient (R^2) = 0.9963. (▲) Series IIB: Regression coefficient (R^2) = 0.9712.

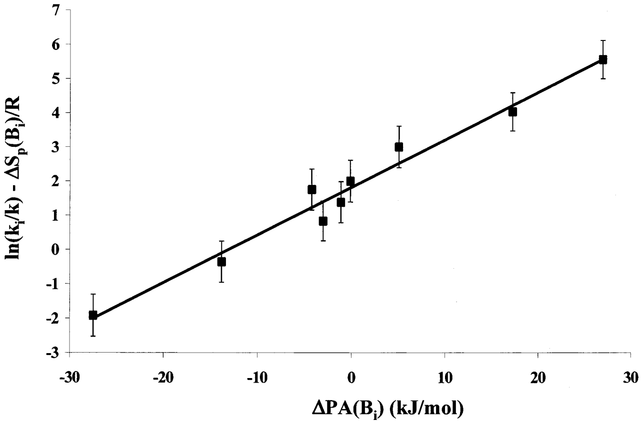

Figure 4. Entropy corrected kinetic method plot, $\ln(k_i/k) - \Delta S_p/R$ versus $\Delta PA(B_i)$, for both series IIA and IIB using urea as the test compound at collision energy 15 eV. The uncertainties shown on the *y*-axis are one standard deviation. Uncertainties of ±5 J/mol·K in ΔS_p are included for each reference base. Regression coefficient (R^2) = 0.9740.

affinity as well as the protonation entropy of the analyte. Armentrout's approach of subtracting an average PA of the reference bases is employed to remove the covariance involved in the second plot. This method provides results that are consistent with values obtained from the literature using the standard method.

Even though we propose the entropy corrected version of the kinetic method as a general approach, we recognize that this method relies on known values of protonation entropies which, in many cases, are not readily available. Even though applications of this method may be hampered by the lack of a reliable source of protonation entropies, valuable information on conformation and other structure features of the analyte might be provided and this would further justify its use.

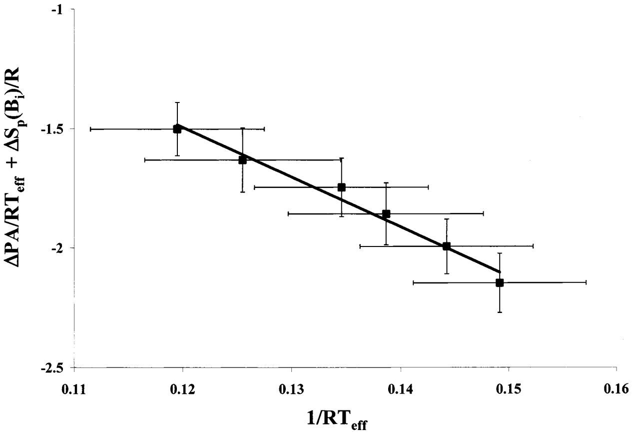

Figure 5. Double plot using the negative value of the intercept (weighted) versus the slope (weighted) obtained from the entropy corrected kinetic method plot for both series IIA and IIB for the determination of the proton affinity and entropy of protonation of urea: plot of $[PA(B) - PA(B_i^{avg})]/RT_{eff} + (\Delta S_p(B)/R)$ versus $1/RT_{eff}$ using the effective temperature values obtained from six different collision energies. The uncertainties shown on both the *x*-axis and the *y*-axis are one standard deviation. Regression coefficient (R^2) = 0.9777.

Conclusions

The kinetic method has been used extensively as an approximate method for determining relative thermochemical properties based on the rates of competitive dissociation of the mass-selected cluster ions. It must be used with care, typically by selecting reference bases and conditions so that entropy changes for the competitive reactions of the reference and unknown compounds are equal. In this study, we present particular cases and demonstrate, by introducing an entropy corrected branching ratio term, that the kinetic method can be applied to structurally dissimilar reference bases. However, this procedure requires additional knowledge in the form of entropic data which may or may not be readily available. In fact, the main use of this version of the kinetic method may be as a source of entropic information in cases where enthalpies are known. Previous work has shown that the kinetic method has value in the areas of ion structure determination, gas-phase chiral distinction, and energy partitioning. It is likely to be even more important for the measurement of ΔS and for making and validating T_{eff} determinations. Future research may include applying the entropy corrected kinetic method to the measurement of the entropy contributions to the dissociation of large biological cluster ions as well as fundamental studies in the area of kinetic energy partitioning in simple organic compounds.

The key features of the present method include (i) explicit correction of the branching ratio for entropy effects, rather than assuming no effects (standard form of the method) or constant differences (extended version); (ii) accurate treatment of uncertainties and linear regression using a statistical approach; (iii) use of Armentrout's average PA subtraction method of avoiding covariance; (iv) use of a protonation entropy procedure to avoid swamping the effects of interest.

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References and Notes

(1) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Chapman and Hall: London, 1973.

(2) Taft, R. W. Gas-Phase Proton-Transfer Equilibria. In *Proton-Transfer Reactions*; Caldin, E., Gold, V., Eds.; Wiley: New York, 1975; pp 31−77.

(3) Gal, J.-F.; Maria, P.-C.; Raczynska, E. D. *J. Mass Spectrom.* **2001**, *36*, 699.

(4) Kebarle, P. Pulsed Electron High-Pressure Mass Spectrometer. In *Techniques of Chemistry*; Farrar, J. M., Saunders, W. H., Jr., Eds.; John Wiley & Sons: New York, 1988; Vol. 20; pp 221−286.

(5) Meot-Ner, M. *J. Phys. Chem.* **1991**, *95*, 6580.

(6) Gorman, G. S.; Amster, I. J. *J. Am. Chem. Soc.* **1993**, *115*, 5729.

(7) Aue, D. H.; Bowers, M. T. Stabilities of Positive Ions from Equilibrium Gas-Phase Basicity Measurements. In *Gas-Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. 2; pp 1−51.

(8) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445.

(9) Hunter, E. P. L.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.

(10) Cooks, R. G.; Kruger, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 1279.

(11) McLuckey, S. A.; Cameron, D.; Cooks, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 1313.

(12) Cooks, R. G.; Patrick, J. S.; Kotiaho, T.; McLuckey, S. A. *Mass Spectrom. Rev.* **1994**, *13*, 287.

(13) Cooks, R. G.; Wong, P. S. H. *Acc. Chem. Res.* **1998**, *31*, 379.

(14) Cooks, R. G.; Koskinen, J. T.; Thomas, P. D. *J. Mass Spectrom.* **1999**, *34*, 85.

(15) Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley-Interscience: New York, 1972.

(16) Drahos, L.; Vekey, K. *J. Mass Spectrom.* **1999**, *34*, 79.

(17) Laskin, J.; Futrell, J. H. *J. Phys. Chem. A* **2000**, *104*, 8829.

(18) Nourse, B. D.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Process.* **1991**, *106*, 249.

(19) Williams, T. I.; Denault, J. W.; Cooks, R. G. *Int. J. Mass Spectrom.* **2001**, *210/211*, 133.

(20) Wenthold, P. G.; Hu, J.; Squires, R. R. *J. Am. Chem. Soc.* **1996**, *118*, 11865.

(21) Vekey, K.; Czira, G. *Anal. Chem.* **1997**, *69*, 1700.

(22) Denault, J. W.; Wang, F.; Cooks, R. G.; Gozzo, F. C.; Eberlin, M. N. *J. Phys. Chem. A* **2000**, *104*, 11290.

(23) Wysocki, V. H.; Kenttamaa, H. I.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1987**, *75*, 181.

(24) Chen, G.; Cooks, R. G.; Bunk, D. M.; Welch, M. J.; Christie, J. R. *Int. J. Mass Spectrom.* **1999**, *185/186/187*, 75.

(25) Tao, W. A.; Zhang, D.; Nikolaev, E. N.; Cooks, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 10598.

(26) Tao, W. A.; Cooks, R. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 757.

(27) Zheng, X.; Augusti, R.; Tao, W. A.; Cooks, R. G. The Kinetic Method: Thermochemical Determinations and Chiral Analysis. In *Encyclopedia on Chemistry and Physics of Gas-Phase Ions*; Gross, M., Caprioli, R., Eds.; Elsevier: New York, 2002; Vol. V. In Press.

(28) Di Donna, L.; Napoli, A.; Sindona, G. *Int. J. Mass Spectrom.* **2001**, *210/211*, 165.

(29) Lardin, H. A.; Squires, R. R.; Wenthold, P. G. *J. Mass Spectrom.* **2001**, *36*, 607.

(30) Cao, J.; Holmes, J. L. *Eur. J. Mass Spectrom.* **2001**, *7*, 243.

(31) Kuntz, A. F.; Boynton, A. W.; David, G. A.; Colyer, K. E.; Poutsma, J. C. *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 72.

(32) Armentrout, P. B. *J. Mass Spectrom.* **1999**, *34*, 74.

(33) Wenthold, P. G.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 11890.

(34) Seburg, R. A.; Squires, R. R. *Int. J. Mass Spectrom. Ion Process.* **1997**, *167*, 541.

(35) Cheng, X. H.; Wu, Z. C.; Fenselau, C. *J. Am. Chem. Soc.* **1993**, *115*, 4844.

(36) Cerda, B. A.; Wesdemiotis, C. *J. Am. Chem. Soc.* **1996**, *118*, 11884.

(37) Cerda, B. A.; Hoyau, S.; Ohanessian, G.; Wesdemiotis, C. *J. Am. Chem. Soc.* **1998**, *120*, 2437.

(38) Nold, M. J.; Cerda, B. A.; Wesdemiotis, C. *J. Am. Soc. Mass Spectrom.* **1999**, *10*, 1.

(39) Armentrout, P. B. *J. Am. Soc. Mass. Spectrom.* **2000**, *11*, 371.

(40) Denault, J. W. Temperature Corrected Kinetic Method for the Determination of Proton Affinities, Entropies of Protonation and Gas-Phase Basicities. Ph.D. Thesis, Purdue University, West Lafayette, IN, 2000.

(41) Armentrout, P. B. Personal Communication. April, 2001.

(42) Armentrout, P. B. Personal Communication. June, 2001.

(43) Cooks, R. G.; Rockwood, A. L. *Rapid Commun. Mass Spectrom.* **1991**, *5*, 93.

(44) Wang, F.; Ma, S.; Zhang, D.; Cooks, R. G. *J. Phys. Chem. A* **1998**, *102*, 2988.

(45) Notario, R.; Castano, O.; Herreros, M.; Abboud, J.-L. M. *J. Mol. Struct.* **1996**, *371*, 21.

(46) Zheng, X.; Tao, W. A.; Cooks, R. G. *J. Am. Soc. Mass Spectrom.* **2001**, *12*, 948.

(47) Meot-Ner, M. *J. Am. Chem. Soc.* **1983**, *105*, 4906.

(48) Sharma, R. B.; Blades, A. T.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 510.

(49) Ervin, K. M. *Int. J. Mass Spectrom.* **2000**, *195/196*, 271.