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Proton Affinities from Dissociations of Proton-Bound Dimers

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Abstract: A kinetic approach to the measurement of gas-phase thermochemical quantities is presented. It relies on generation and dissociation in a reverse geometry mass spectrometer of a dimeric ion $A_1XA_2^{+(-)}$ where A_1 and A_2 are species whose affinity for X is of interest. The underlying assumptions of the data treatment and limitations of the technique are discussed. A linear relationship between the logarithm of the peak height ratios of the product ions in the dissociation of a proton-bound dimer vs. proton affinity is observed for a series of alkylamines, substituted anilines, and substituted pyridines, with correlation coefficients of 0.95, 0.97, and 0.98, respectively. In general, proton affinities obtained by the kinetic measurement agree within 0.3 kcal mol^{-1} with values obtained by conventional equilibrium measurements although the experiment requires careful choice of reference compounds. Examples of determinations for which literature values do not exist are PA(phenylethylamine) = 218.7 ± 0.3 kcal mol^{-1} and PA(quinoline) = 225.8 ± 0.3 kcal $mole^{-1}$. Extensions of the technique to the measurement of gas-phase acidities, hydride affinities, and metal cation affinities are described.

Introduction

Relative gas-phase proton affinities are accessible in an experiment[1] in which two bases, B_1 and B_2, are bound by a proton and the resulting dimer ion is dissociated (eq 1). This kinetic

$$B_1{\cdots}H^+{\cdots}B_2 \rightarrow B_1H^+ + B_2 \qquad (1a)$$

$$B_1{\cdots}H^+{\cdots}B_2 \rightarrow B_1 + B_2H^+ \qquad (1b)$$

procedure, based on the relative rates of (1a) and (1b), stands in contrast to established methods[2] in which the position of equilibrium is measured, either directly or from the rates of the forward and reverse reactions (eq 2). Increased awareness of

$$B_1H^+ + B_2 \rightleftarrows B_1 + B_2H^+ \qquad (2)$$

the significance of gas-phase thermochemical parameters increases the importance of new methods of obtaining this data, particularly for small samples, which may be of high molecular weight and unavailable in a pure state.

The method presented here employs, for example, a chemical ionization source to generate the proton-bound dimer and a reverse sector mass spectrometer, viz. a mass-analyzed ion kinetic energy spectrometer (MIKES),[3] to select the dimer and to record the mass spectrum of its fragmentation products. The dissociations (eq 1) may be spontaneous, that is the dimer ion may be metastable, or dissociation can be induced in a glancing collision at kilovolt energy with a gaseous target. The basis for the method is (i) for similar species B_1 and B_2, the competitive fragmentations of the dimer into the protonated monomers should have similar frequency factors (entropy changes) and (ii) since the fragmentations of the dimer are simple cleavages, the reactions should have zero or very small reverse activation energies.[4] If these conditions hold, the rates of the fragmentations are controlled by the relative activation energies of each reaction channel, the difference in which is equivalent to the difference in proton affinities (Figure 1). If secondary dissociations do not occur, then the abundances of the fragment ions B_1H^+ and B_2H^+ will be determined by the rates of reactions shown in eq 1. Hence, the relative peak heights of the fragment ions can indicate the relative proton affinities of the parent bases.

The purposes of this paper are to indicate the probable generality of this concept in ordering gas-phase thermochemical values, to quantitate the method, and to explore its limitations. The first point is addressed with examples which indicate that gas-phase acidities and hydride affinities are also accessible. Quantitation is addressed in the context of several series of closely related compounds, and some of the limitations on application of the method will be presented in relation to studies on some ketones.

Experimental Section

Experiments were performed on a MIKE spectrometer,[3] a reverse geometry mass spectrometer fitted with a chemical ionization (CI) source. Methane and isobutane were used as reagent gases at source pressures of 0.2–0.5 torr, as measured on a MKS Baratron capacitance manometer, and a nominal source temperature of 425 K measured by an iron-constantan thermocouple in contact with the source block. Unless otherwise specified, nitrogen was used as the collision gas in those ex-

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(1) For a preliminary communication, see: Cooks, R. G.; Kruger, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 1279.

(2) (a) Aue, D. H.; Bowers, M. T. "Gas-Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, pp 2–15. (b) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445. (c) Henderson, W. G.; Taagepera, M.; Holtz, D.; McIver, R. T., Jr.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 4728.

(3) (a) Kondrat, R. W.; Cooks, R. G. Amy, J. W.; Baitinger, W. E.; Ridley, T. Y. *Anal. Chem.* **1973**, *45*, 1023A.

(4) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, R. G. "Metastable Ions"; Elsevier: Amsterdam, The Netherlands, 1973.

(5) Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 2906.

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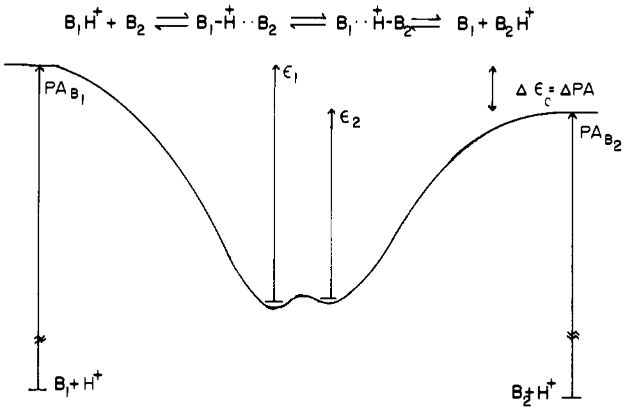


Figure 1. A potential energy surface for the formation and dissociation of a proton-bound dimer of two bases.[5] Also shown is the relationship between the difference in activation energies $\Delta\epsilon_0$ and the difference in proton affinities (ΔPA).

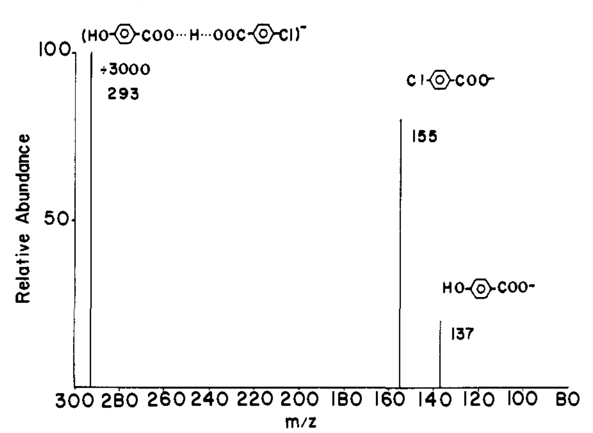


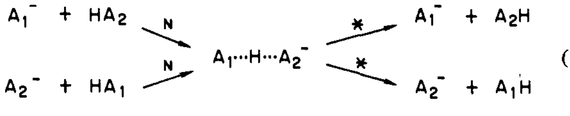
Figure 2. The MIKE spectrum of the unsymmetrical negatively charged proton-bound ion of the *p*-chlorobenzoate and the *p*-hydroxybenzoate anions (*m/z* 293). The peak at *m/z* 137 corresponds to the *p*-hydroxybenzoate anion and its lower intensity is indicative of its larger proton affinity.

periments involving collision-induced dissociations (CID) at an indicated pressure on a Bayard-Alpert gauge of 4 × 10^{-5} torr, with an estimated collision cell pressure of (1-2) × 10^{-3} torr. Ion accelerating voltages of 7 kV and analogue detection with a Channeltron electron multiplier were used in all experiments. Samples were prepared by mixing two or more compounds, placing the mixture into a glass capillary tube, and introducing it into the source via a direct insertion probe. Negative ions were recorded by using the same conditions as positive ions with the appropriate changes in analyzer and accelerating voltage polarities.

Abundance ratios of the fragment ions in the MIKE or MIKE/CID spectra were reproducible to within ±10% and the logarithm of the fragment ion abundances to within ±5%.

Results and Discussion

Scope of the Method. Figure 2 shows the products of dissociation of the negatively charged unsymmetrical proton bound dimer (*m/z* 293) formed from the *p*-chlorobenzoate and the *p*-hydroxybenzoate anions. This MIKE spectrum shows that just two reactions occur (eq 3) and that they correspond to formation



$$\begin{matrix} A_1^- + HA_2 & \xrightarrow{N} & & \xrightarrow{*} & A_1^- + A_2H \\ & & A_1\cdots H\cdots A_2^- & & \\ A_2^- + HA_1 & \xrightarrow{N} & & \xrightarrow{*} & A_2^- + A_1H \end{matrix} \qquad (3)$$

of the anions themselves, reversing the process whereby the dimer is formed (the asterisk indicates a metastable ion dissociation; N indicates a third body).

The ratio of peak heights observed (Figure 2) for the *p*-chlorobenzoate vs. the *p*-hydroxybenzoate anions suggests that the latter has the greater proton affinity. This is based on the argument developed in the introduction and supported by earlier data[1] on alkylamines. Independent gas-phase acidity results[6] confirm the conclusion that the proton affinity of *p*-chlorobenzoate is smaller than that of *p*-hydroxybenzoate.[7]

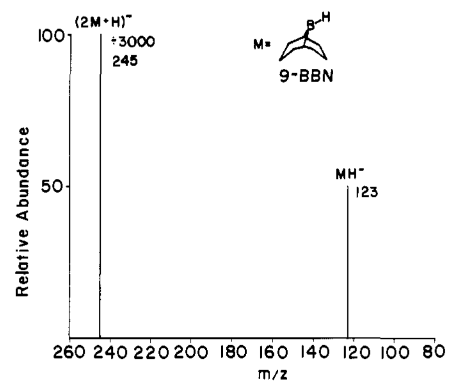
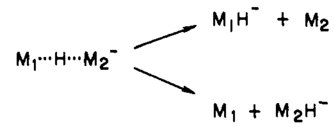


Figure 3. The MIKE spectrum of the negatively charged symmetrical hydride-bound dimer of 9-borabicyclo[3.3.1]nonane (9-BBN). The peak at *m/z* 123 corresponds to the borohydride anion.

This qualitative result, together with those given below for alkane carboxylic acids, shows that the method can be applied in the case of negatively charged as well as positively charged ions. Its usefulness in both types of applications will be shown to be comparable.

The example just discussed is seen to be closely analogous to the positive ion case when the dimer $(A_1\cdots H\cdots A_2)^-$ is considered formally as the proton-bound structure $A_1^-\cdots H^+\cdots A_2^-$. It seems likely, however, that entirely different applications will be possible on the basis of other weakly bonded cluster ions of the general form $X\cdots Y\cdots Z^{+(-)}$. An example of this is the determination of hydride affinities by using reaction 4. The feasibility of this



$$M_1\cdots H\cdots M_2^- \begin{cases} \rightarrow M_1H^- + M_2 \\ \rightarrow M_1 + M_2H^- \end{cases} \qquad (4)$$

approach is indicated by results for the hydride-bound dimer of 9-borabicyclo[3.3.1]nonane (Figure 3). A single fragment peak is observed for this symmetrical ion, and it corresponds to the expected borohydride. This particular application has not yet been developed further. The ready formation[9] in secondary ion mass spectrometry (SIMS) of metal bound clusters $M_1\cdots C^+\cdots M_2$, when M is an organic molecule and C^+ a transition-metal cation, makes accessible other interesting measurements.

Quantitation. Although this experiment is concerned with the unimolecular dissociations of isolated ions, it is convenient to consider the reactant ions as having an effective temperature (*T*) for which the unimolecular rate constant (*k*) can be expressed in the usual way[10] as in eq 5, where *Q* is the partition function

$$k = \frac{RT}{h}\frac{Q^*}{Q}e^{-\epsilon_0/RT} \qquad (5)$$

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[6] Yamdagni, R.; McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1974**, *96*, 4035.

[7] The D(A-H) - EA(A) values of *p*-chlorobenzoic acid and *p*-hydroxybenzoic acid are 18.65 kcal mol^{-1} ($D(A^--H^+)$ = 332.2 kcal mol^{-1}) and 19.05 kcal mol^{-1} ($D(A^--H^+)$ = 332.6 kcal mol^{-1}), respectively. The gas-phase acidity of a particular species AH is expressed as its heterolytic bond dissociation energy $D(A^--H^+)$ which is equivalent to the proton affinity of A^- as shown in eq a and b.

$$A^- + H^+ \rightarrow AH \quad PA(A^-) \equiv -\Delta H \qquad (a)$$

$$AH \rightarrow A^- + H^+ \quad \Delta H = D(A^--H^+) = PA(A^-) \qquad (b)$$

The bond dissociation energy can also be written as

$$D(A^--H^+) = D(A\text{-}H) - EA(A) + IP(H) \qquad (c)$$

where *D*(A-H) is the homolytic bond dissociation energy, EA(A) is the electron affinity of the species A, and IP(H) is the ionization potential of the hydrogen atom. Since IP(H) is constant (313.6 kcal mol^{-1}),[8] relative gas-phase acidities are often expressed as *D*(A-H) - EA(A).

[8] McMahon, T. B.; Kebarle, P. *J. Am. Chem. Soc.* **1977**, *99*, 2222.

[9] Day, R. J.; Unger, S. E.; Cooks, R. G. *Anal. Chem.* **1980**, *52*, 557A.

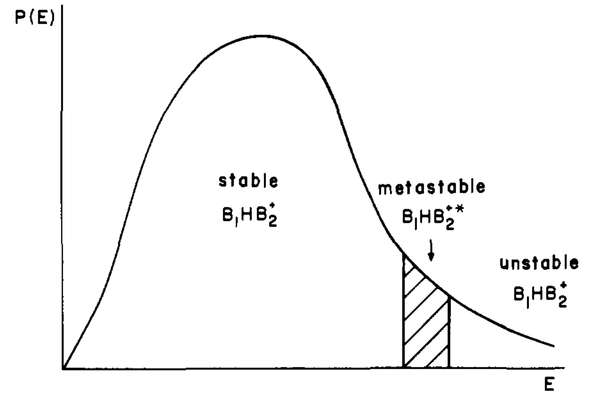

Figure 4. A schematic representation of the internal energy distribution P(*E*) vs. *E* of the dimer ions extracted from the chemical ionization source. The shaded area labeled metastable $B_1HB_2^+$ indicates the energy range for the observation of metastable decomposition.

of the ion, Q^* is that for the activated complex, and ϵ_0 is the activation energy. For the competing reactions a and b of eq 1

$$\ln (k_1/k_2) = \ln Q_1{}^*Q_2/Q_2{}^*Q_1 + \Delta\epsilon_0/RT \qquad (6)$$

where $\Delta\epsilon_0$ is the difference in activation energies for reactions 1a and 1b. Since the reactions proceed from the same reactant

$$Q_1 = Q_2 \qquad (7)$$

and since the activated complexes for reactions 1a and 1b differ most significantly in the hydrogen bond frequencies

$$Q_1{}^*/Q_2{}^* \simeq \nu_1/\nu_2 \qquad (8)$$

so

$$\ln (k_1/k_2) \simeq \ln \nu_1/\nu_2 + \Delta\epsilon_0/RT \qquad (9)$$

where ν_1 and ν_2 are the vibrational frequencies of the hydrogen bonds in the proton-bound dimer. When these frequencies are equal, a simple relationship connects the ratio of the rate constants and the difference in proton affinities for the two reactions.

$$\ln (k_1/k_2) = \Delta\epsilon_0/RT \qquad (10)$$

When this relationship holds, a plot of ln (k_1/k_2) vs. ϵ_0 will result in a straight line of slope $1/RT$. It is important to note that T here is not the temperature of the dimer ions in the source (which are generally considered to be thermalized under normal CI conditions[11]) but is an effective temperature of those dimer ions which undergo unimolecular dissociation in a selected region. Since a kinetic selection is being made, the magnitude of the observed effective temperature is determined by the ion structure and the time scale of the instrument for the observation of metastable transitions.[12] A schematic representation of the internal energy distribution of a dimer ion population in the source is shown in Figure 4. The shaded area indicates the energy range for the observation of a metastable decomposition of $B_1\cdots H\cdots B_2^+$ in the second field-free region of the mass spectrometer. Since metastable ion internal energies are determined by the nature of the ion and the time scale of the instrument, the effective temperature is expected to be insensitive to variations in source conditions when internal energies are broadly populated[13] as they are under CI conditions. Changes in the ion source temperature over a range of 150 °C, for example, alter the absolute intensities of the product ions by shifting the internal energy distribution of the dimer ions in the source but are observed not to result in changes in the product distribution for several substituted pyridines. Furthermore, the product distribution for substituted anilines is observed not to vary between studies using methane as reagent gas and those using isobutane. Finally, in studies with several substituted pyridines, no significant variations in the product distribution are observed when the source pressure is varied from 0.1 to 0.8 torr, despite marked changes in the absolute intensities of the product ions.[14]

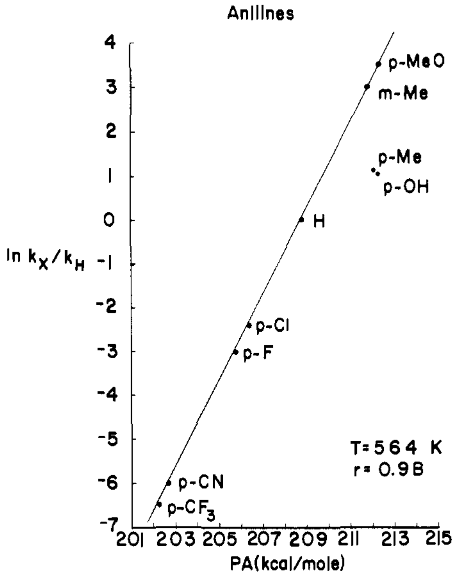

Figure 5. Logarithm of relative rates of dissociation from proton-bound dimers of a series of substituted anilines vs. proton affinity. All rates k_X where X represents the substituent are relative to aniline.

Results from the MIKE spectra for a series of substituted anilines using methane as the reagent gas are plotted in Figure 5. Employing the ratio of the substituted aniline peak height over the protonated aniline peak height $[B_XH^+]/[B_HH^+]$ for k_X/k_H and plotting against proton affinity[15] gives a straight line with a correlation coefficient of 0.98 and an effective temperature, as determined from the slope, of 564 K. The plot is constructed in a stair-step fashion. For example, the peak ratio of protonated *p*-fluoroaniline vs. protonated aniline is 0.050. The peak height ratio of protonated *p*-cyanoaniline vs. protonated *p*-fluoroaniline is also 0.050. The ratio of protonated *p*-cyanoaniline vs. protonated aniline is then taken to be 0.0025 or ln $(k_{CN}/k_H) = -6.0$. This allows bases with large differences in proton affinity to be related quantitatively. Bases with relatively large proton affinity differences (typically greater than 2 kcal mol^{-1}) cannot be compared accurately in a single experiment, as is also true with equilibrium methods.[2a] This is because the spectra of such dimers either show only one peak, corresponding to the stronger base, or exhibit abundance ratios that are so large that they cannot be accurately determined.

Figure 6 shows the data obtained from the MIKE spectra of a series of substituted pyridines. The plot of ln (k_X/k_H) vs. proton affinity,[2a] where k_X represents the peak height of a substituted pyridine and k_H the peak height of pyridine, results in a line with a correlation coefficient of 0.97 and an effective temperature of 425 K. As with the aniline data, the graph is constructed in a

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(10) Robinson, P. J.; Holbrook, K. A. "Unimolecular Reactions"; Wiley-Interscience: London, 1972.

(11) Field, F. H. "Ion-Molecule Reactions"; Franklin, J. L., Ed.; Plenum Press: New York, 1972; Vol. I, p 264.

(12) McLafferty, F. W.; Wachs, T.; Lifschitz, C.; Innorta, G.; Irving, P. *J. Am. Chem. Soc.* **1970**, *92*, 6867.

(13) Levsen, K. "Fundamental Aspects of Organic Mass Spectrometry"; Verlag Chemie: New York, 1978; pp 120–123.

(14) A reviewer has asked if the ions are being activated by collision during acceleration from the source. The results just quoted suggest not (compare ref 2b), but the mode of excitation is immaterial provided the time delay before sampling is not varied.

(15) Hartman, K. N.; Lias, S.; Ausloos, P.; Rosenstock, H. M.; Schroyer, S. S.; Schmidt, C.; Martinsen, D.; Milne, G. W. "A Compendium of Gas Phase Basicity and Proton Affinity Measurements"; 1979; NBSIR 79-1777.

(16) Lalau, C. "Topics in Organic Mass Spectrometry"; Burlingame, A. L.; Ed.; Wiley-Interscience: New York, 1970.

(17) Cumming, J. B.; Kebarle, P. *Can. J. Chem.* **1978**, *56*, 1.

(18) (a) Hunt, D. F.; Sethi, S. K. *J. Am. Chem. Soc.* **1980**, *102*, 6953. (b) Keough, T.; Destefano, A. J., to be submitted. (c) Cameron, D.; Cooks, R. G., submitted for publication.

(19) Cameron, D.; Cooks, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 3162.

(20) Meot-Ner, M.; Hunter, E. P.; Field, F. H. *J. Am. Chem. Soc.* **1977**, *99*, 5576.

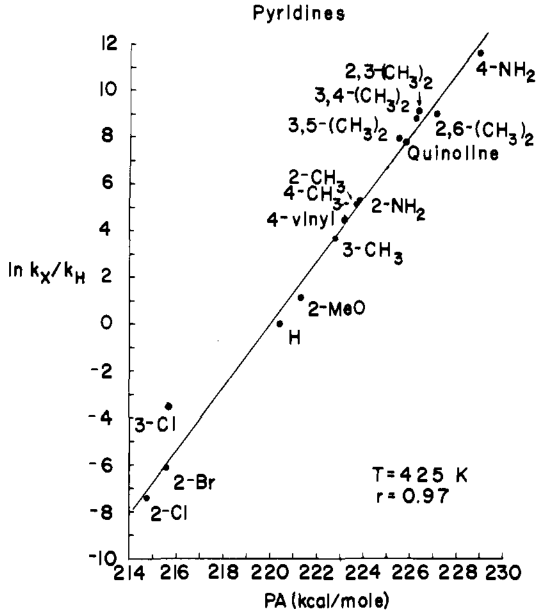

Figure 6. Logarithm of the relative rates of dissociation from proton-bound dimers of a series of substituted pyridines vs. proton affinity. All rates k_X where X represents the substituent are relative to pyridine.

stair-step fashion. For example, the peak height ratio of protonated 3-methylpyridine vs. protonated pyridine is 39. The ratio for protonated 2-aminopyridine vs. protonated 3-methylpyridine is 4.6. The ratio of protonated 2-aminopyridine vs. protonated pyridine is then taken to be 180 or $\ln (k_{2\text{-NH}_2}/k_H) = 5.2$. Illustrating further, both the peak height ratios of protonated 2-methyl and 4-methylpyridines vs. protonated 2-aminopyridine are 0.90. The peak height ratios for the protonated forms of both 2- and 4-methyl-substituted pyridines vs. protonated pyridine are therefore taken to be 160 or $\ln (k_{2\text{-CH}_3}/k_H)$ and $\ln (k_{4\text{-CH}_3}/k_H) = 5.1$.

The proton affinity of quinoline was determined by using the data in Figure 6 and serves as an illustrative case for the quantitative determination of an unknown proton affinity. In a direct comparison with pyridine, the protonated pyridine peak in the MIKE spectrum was negligible in comparison to that of protonated quinoline, indicating a large proton affinity difference. A comparison with 2-aminopyridine (PA = 223.8 kcal mol^{-1})[2a] resulted in a peak height ratio for $(\text{quinoline} + \text{H})^+/(\text{2-aminopyridine} + \text{H})^+$ of 9.5, yielding a proton affinity value of 225.2 kcal mol^{-1}. A comparison with 3,4-lutidine (PA = 226.2 kcal mol^{-1})[2a] resulted in a peak height ratio of 0.44 for $(\text{quinoline} + \text{H})^+/(\text{3,4-lutidine} + \text{H})^+$, yielding a proton affinity value of 225.8 kcal mol^{-1}. The smaller proton affinity difference between quinoline and 3,4-lutidine than with quinoline and 2-aminopyridine is reflected in the smaller peak height difference in the latter experiment and indicates that the proton affinity of quinoline is more accurately measured by comparison with 3,4-lutidine. Therefore, the proton affinity of quinoline is assigned a value of 225.8 kcal mol^{-1} with an estimated error of ±0.3 kcal mol^{-1}.

A plot of corrected $\ln (k_1/k_2)$ values vs. proton affinity for a series of proton-bound dimers of alkylamines and pyridine is shown in Figure 7, where k_2 represents the abundance of protonated *n*-propylamine in each case. The reagent gas in these studies was methane. To correct for the discrimination effect from the electron multiplier detector,[16] the ion abundance ratio, B_1H^+/B_2H^+, is multiplied by the mass ratio $(m_2 + 1)/(m_1 + 1)$. The kinetic energy effect is usually the largest factor in detector discrimination, and fragment ions in a MIKES experiment have kinetic energies which depend linearly on the mass of the ion. Detector discrimination, therefore, increases in significance as the difference in mass of the fragment ions increases and is more significant here than in the aniline and pyridine experiments. Using the corrected data in the plot of Figure 7 results in a correlation coefficient of 0.95 and an effective temperature of 243 K.

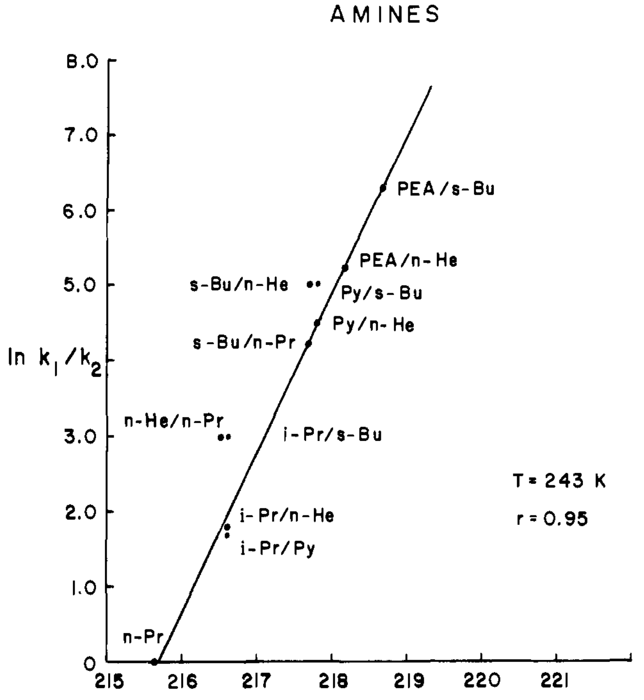

Figure 7. Logarithm of the corrected abundance ratio vs. proton affinity for a series of alkylamine proton-bound dimers. The ratios are corrected for kinetic energy discrimination by the detector and referenced to *n*-propylamine. The proton affinity plotted is that of the base shown in the numerator of the ratio.

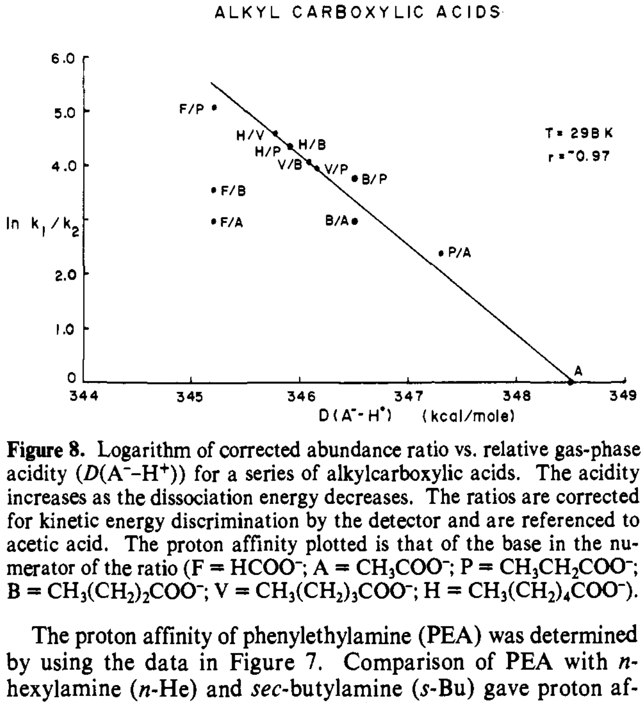

Figure 8. Logarithm of corrected abundance ratio vs. relative gas-phase acidity ($D(\text{A}^--\text{H}^+)$) for a series of alkylcarboxylic acids. The acidity increases as the dissociation energy decreases. The ratios are corrected for kinetic energy discrimination by the detector and are referenced to acetic acid. The proton affinity plotted is that of the base in the numerator of the ratio ($\text{F} = \text{HCOO}^-$; $\text{A} = \text{CH}_3\text{COO}^-$; $\text{P} = \text{CH}_3\text{CH}_2\text{COO}^-$; $\text{B} = \text{CH}_3(\text{CH}_2)_2\text{COO}^-$; $\text{V} = \text{CH}_3(\text{CH}_2)_3\text{COO}^-$; $\text{H} = \text{CH}_3(\text{CH}_2)_4\text{COO}^-$).

The proton affinity of phenylethylamine (PEA) was determined by using the data in Figure 7. Comparison of PEA with *n*-hexylamine (*n*-He) and *sec*-butylamine (*s*-Bu) gave proton affinities of 218.2 and 218.7 kcal mol^{-1}, respectively. Independent data are not available, but these values are reasonable considering the trend of proton affinities from aniline (208.8 kcal mol^{-1}) to benzylamine (214.5 kcal mol^{-1}).[15] The value obtained with *n*-He is likely to be less accurate due to the larger proton affinity difference involved in this study. The proton affinity value assigned to PEA, therefore, is 218.7 kcal mol^{-1} with an estimated error of ±0.3 kcal mol^{-1}.

Gas-phase acidity measurements are also amenable to this type of treatment. Figure 8 shows a plot of the logarithm of the corrected metastable abundance ratios of formic, acetic, propionic, and butyric acids using isobutane as reagent gas vs. heterolytic bond dissociation energies as determined by Kebarle.[17] Omitting the results for formic acid, a least-squares fit of the data yields a correlation coefficient of 0.97 with an effective temperature of 298 K. The data for formic acid fall off the line, probably due to a combination of unfavorable factors including measurement against acids of substantially different acidity, different entropy factors, and different transmission efficiencies associated with fragments whose mass ratio differs substantially from unity.

The relative gas-phase acidities of valeric and hexanoic acids have been determined from the plot of Figure 8. Comparing valeric acid to propionic and butyric acids, values of 346.2 and 346.0 kcal mol^{-1}, respectively, are obtained for $D(A^- - H^+)$. Comparing hexanoic acid to propionic and butyric acids gives a value of 345.9 kcal mol^{-1} from both measurements. Comparing hexanoic to valeric acid gives a value of 345.8 kcal mol^{-1} for hexanoic acid. The gas-phase acidity values assigned for valeric and hexanoic acids are 346.1 and 345.9 kcal mol^{-1}, respectively, each with an estimated error of ±0.3 kcal mol^{-1}. No literature values for these acids are available for comparison.

A series of experiments using a collision gas in the post magnet field free region was performed on these acids to determine the effect of collision-induced dissociation (CID) upon the effective temperature of the dimer ion. The CID abundance ratios of propionic, butyric, and acetic acids correlated quite well with relative gas-phase acidities, giving a correlation coefficient of 0.999 and an effective temperature of 543 K. Comparing hexanoic acid to butyric and valeric acids gave gas-phase acidity values of 345.6 and 345.7 kcal mol^{-1}, respectively. Agreement between the metastable ion and CID results in good, differing at most by 0.3 kcal mol^{-1}. Although the correlation between the logarithm of the abundance ratios and relative gas-phase acidities is slightly better for the CID experiments, the metastable ion data are approximately 1.5 times more sensitive to differences in acidity as determined by a comparison of the slopes. As expected, the effect of collision-induced dissociation is to increase the internal energy of the dimer as reflected by T and consequently to flatten the slope. Both the absolute peak intensities, as well as the ratio of peak heights, are more precisely measurable in the CID experiments. These latter measurements are also useful in providing a complete dissociation spectrum which allows one to test the structure of the dimer ion (structures other than the proton-bound dimer give complex MIKE spectra while the proton-bound dimers yield just the products A_1^- and A_2^-).

Preliminary results on some dimers comprised of a substituted aniline and a substituted pyridine indicate that the method is applicable, at least qualitatively and in some cases quantitatively, to such systems. For example, the data from the MIKE spectra of 2-cyano-, 3-cyano-, and 4-cyanopyridine bound to protonated *p*-chloroaniline, when plotted against proton affinity, result in a straight line. Although for every mixed-base dimer tested the product peak heights followed the proton affinities qualitatively, a linear correlation with $\ln k_1/k_2$ appears to be obtained only when each dimer species is of the same functional type. That is, in this case, when each point is determined from an (aniline + pyridine + H)$^+$ dimer.

Conclusion

In summary, the kinetic approach can be utilized in obtaining thermochemical information via the study of dimers bound by a selected species. Direct experimental evidence that proton-bound dimers can be used in determinations of gas-phase thermochemistry is to be found in a large collection of data[2a] where equilibrium measurements (as opposed to the present kinetic measurements) were used. These authors' results show generally excellent parallels between data obtained for the average proton affinities of two bases and their molecular pair proton affinity (MPPA) where MPPA = $-\Delta H$ of reaction 11.

$$B_1 + B_2 + H^+ \rightarrow (B_1HB_2)^+ \qquad (11)$$

Specifically, the measured MPPA values for some 70 proton-bound dimers of nitrogen bases differ from the average proton affinity of the bases composing the dimer by 20.9 kcal mol^{-1} with an average standard deviation of 1.1 kcal mol^{-1} (that is, MPPA − average PA = 20.9 kcal mol^{-1}). These results indicate that in principle, quantitative determinations of relative thermochemical quantities are possible by using proton-bound dimers, and our data support this expectation. It cannot be expected that the sites through which hydrogen bonding occurs in the dimer will necessarily correspond to the site(s) of protonation of the free bases. This could lead to a divergence of the results obtained by the kinetic and the thermochemical method. Determination of the site of cation attachment in aromatic bases and in the dimers is under scrutiny.[18]

Some of the factors which could restrict application of this simple and rapid determination have been uncovered. In making proton affinity measurements the primary prerequisite for application of this technique is the formation of a dimer with the proton-bound structure involving two weak hydrogen bonds. Evidence for the proton-bound structure is the appearance of only two fragment peaks in the MIKE spectrum (and its CID counterpart) corresponding to the masses of the expected product ions. The appearance of alternate fragmentations indicates the possibility of a covalently bonded dimer structure. This is the case, for example, for the benzyl acetate (2M + 1)$^+$ dimer which has been explicitly shown to be covalently bonded[19,20] and as such is not suited to the present type of study.

In some situations mixtures of ion structures which include the proton-bound dimer may be generated. This can be recognized from the MIKE/CID spectrum and need not preclude qualitative thermochemical determinations. For example, several unsymmetrical ketone dimers have been studied on a preliminary basis by using methane as the reagent gas. The MIKE spectra for some of these ketone dimer combinations show relatively abundant $B^{+\cdot}$ ions in addition to the usual BH^+ ions, suggesting the possibility of covalent bond formation. Thus, the MIKE spectrum of the (2M + 1)$^+$ dimer of acetone and 2-pentanone shows a peak at *m/z* 58, corresponding to $B^{+\cdot}$ in addition to the expected BH^+ ions at *m/z* 87 and *m/z* 59, with an intensity one-third that of *m/z* 59 and one-fifth that of *m/z* 87. In cases such as this, the peak heights of the BH^+ ions follow the proton affinities qualitatively but not quantitatively. Where the proton-bound dimer ion structure is generated, as in the cases of the alkylamines, anilines, and carboxylic acids, quantitative results are obtained, provided the method is limited to studies which encompass a series of similar dimers. Otherwise, the technique can be used successfully to estimate unknown proton affinities by bracketing within established proton affinities of two reference compounds.

The effective temperature, as obtained from the plot of $\ln k_1/k_2$ vs. proton affinity, is not to be used to evaluate temperature effects on acidity and basicity. However, it behaves as expected as a measure of internal energy. In particular, metastable ions have lower effective temperatures than their counterparts after collisional activation. They are therefore more sensitive to small differences in proton affinity and more useful than CID experiments for distinguishing bases of similar strength. The structural factors controlling effective temperature are not understood, and this question is under study by using dimers comprised of bases of different functional classes.

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