Gas-phase equilibrium affinity scales and chemical ionization mass spectrometry

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I. INTRODUCTION

The technique of chemical ionization mass spectrometry (CIMS), developed for general use by Field and co-workers (1–3), has proved to be an extremely useful alternative to the traditional electron ionization mass spectrometry (EIMS). Rather than forming the analyte ions by the "hard" electron ionization process, the mass spectrometrist can use a limited set of reagent ions to react with the analyte in the gas phase. Ions formed as products of these bimolecular ion/molecule reactions are usually much less energetic than those formed in the EI process, resulting in less fragmentation of the analyte ion. In the ideal case, CIMS produces an ion with a mass closely related to the molecular mass, as the base peak in the spectrum, plus a limited number of fragment ions that provide structural information. With the proper CI reagent gas, the amount of fragmentation can be varied, or specific structural features detected and located within the compound. In practice, however, the exact nature of the parent ion (M + H, M − H, M, or M + reagent ion) varies with both the reagent gas and the structural features of the analyte. Likewise, the amount of fragmentation products is in part related to the energetics of the ion/molecule reaction (2,4).
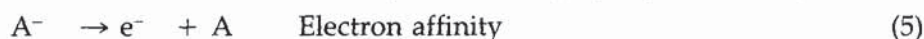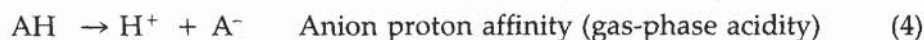
This article focuses on the energetics of some of the reactions commonly used in CIMS, by examining the various gas-phase equilibrium affinity scales that have been developed in the last two decades. These scales provide much of the basis for our current knowledge of ion thermochemistry pertinent to CIMS. Their establishment, current uncertainties involving them, and practical considerations related to CIMS and other MS techniques are discussed. Some possible new directions will be mentioned. A more general review of CIMS has been done recently by Harrison (5), and reviews on negative ion CIMS (6) and ammonia CIMS (7) have appeared recently in this journal.

In EIMS, interpretation and prediction of spectra is facilitated by knowledge of the energetics of the processes involved. For cations, these thermochemical data have largely been obtained from measurement of ionization energies and appearance energies (the threshold energetics for reactions 1 and 2) by using appropriately configured mass spectrometers.

$$AB + e^- \quad \rightarrow \quad AB^{+\cdot} + 2e^- \qquad\qquad (1)$$

$$AB + e^- \quad \rightarrow \quad A^\cdot + B^+ \text{ and } 2e^- \qquad\qquad (2)$$
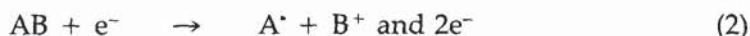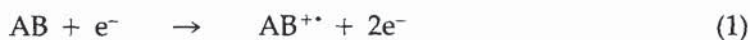
Such measurements provide the heat of formation of the cation and the ionization energy of the neutral (or conversely, the recombination energy of the ion). With these values, the thermochemistry of other processes can be calculated, and a reasonable estimate of the internal energy of the ions obtained (8).

Although a wide variety of ion/molecule reactions has been used in CIMS, the majority of the reports in the literature involve a limited set of reagent ions. These commonly result in Brønsted acid/base reactions, electron attachment, and to a more restricted extent, Lewis acid/base reactions, especially of metal ions (5). The energetics associated with these chemical properties can be written as shown in Eqs. (3)–(7), where they are defined as affinities:

$$BH^+ \rightarrow H^+ + B \qquad \text{Proton affinity (gas-phase basicity)} \qquad (3)$$

$$AH \ \rightarrow H^+ + A^- \qquad \text{Anion proton affinity (gas-phase acidity)} \qquad (4)$$

$$A^- \ \rightarrow e^- \ + A \qquad \text{Electron affinity} \qquad (5)$$

$$AX^- \rightarrow X^- \ + A \qquad \text{Anion affinity} \qquad (6)$$

$$BM^+ \rightarrow M^+ + B \qquad \text{Cation affinity} \qquad (7)$$

the enthalpy of detachment of an ionic species from some compound (neutral or charged). As reactions (3)–(7) are written, the numeric quantity is positive. The name given is for the enthalpy change, whereas the phrase in parentheses refers to the free energy quantity involved. Unlike reactions (1) and (2), however, the energetics for reactions (3)–(7) often are not measured directly as threshold values for the reactions as written. Instead, to determine the affinity, an equilibrium is set up between two of the neutral species and their respective ionized forms, for example:

$$B_1 + B_2H^+ \rightleftarrows B_1H^+ + B_2 \qquad\qquad (8)$$
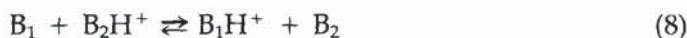
Using the various mass spectrometric techniques, the relative abundances of the two ions can be determined under conditions where the process should be at equilibrium. If the relative partial pressures of the two neutrals within the vacuum system are known, then the equilibrium constant K_8 can be calculated, and thus $\Delta G(8) = -RT \ln(K_8)$. Equilibration of B_2 and B_2H^+ with B_3 and B_3H^+ under identical conditions, and so forth, leads to development of an extensive "ladder" of relative free energies. Such ladders are usually constructed with multiple paths between any two compounds, which serve to verify each individual measurement. The construction of such ladders, and assignment of the relative values, has in the past been by inspection. A computer program for determining the best fit of the assigned relative values to the experimental equilibria, and assessment of possible bad values and poor construction, is currently under development (9).

The techniques commonly used for determination of these equilibria are ion cyclotron resonance (ICR) spectrometry (10) [or in its latest form, Fourier transform ICR mass spectrometry (11)], flowing afterglow (12), and pulsed chemical ionization mass spectrometry (13). The latter, also referred to as pulsed high pressure mass spectrometry, is a modification of CIMS in which the ionization beam is pulsed, and the time response of the ions monitored, to determine whether equilibrium is established. ICR experiments are carried out at pressures of 1×10^{-6} torr or less, and in a time range of seconds, where termolecular collisions are not common, whereas the latter two techniques operate at bath gas pressures of about 1 torr and in time ranges of a few milliseconds at most. The techniques will not be further reviewed here. To convert from the relative free energies obtained in this fashion to relative enthalpies, either the temperature dependence of the various equilibria must be determined (14), and ΔH obtained from a van't Hoff plot, or the entropies for the reactions may be estimated from statistical mechanics (15,16). For proton transfer reactions such as shown in Eqs. (3) and (4), it is primarily the change in rotational symmetry and loss of internal rotations that determine the entropy change; these are relatively easy to calculate. For the anion and cation affinities, it is more difficult to obtain entropies from statistical mechanics (17). In the gas phase, however, the entropy change for *equilibrium* processes such as Eq. (8) is usually fairly small and often can be neglected at the kcal/mol uncertainty level.

Once a relative scale of affinities or free energy changes is obtained, it must be "anchored" to some absolute value. If the absolute value of any one of the species in the scale is known, then absolute values can be assigned to all of them. Ideally, several absolute values for species throughout the range of the scale should be used to check for errors in the relative scale values. It has been the case that a net compression or error in the relative scale has been detected this way (see Section II.B).

The uncertainties of the *relative* affinities from equilibrium scales are commonly 0.1–0.2 kcal/mol, for one value to another, but about 2.0–2.5 kcal/mol in an *absolute* sense, due to the uncertainties commonly encountered in the anchoring data. The absolute uncertainty is the one quoted in most compilations and is the uncertainty used to assign heats of formation to the ions involved. When using the affinity values from these scales, one needs to be aware that the type of usage determines the size of the uncertainty.

Another desirable situation is the confirmation of any of these scales by a second technique (ICR vs. CIMS, either of these vs. some absolute measurement), ideally for a number of cases over the range of the scale. This was done for several of the scales mentioned below.

The current most comprehensive compilation of such equilibrium affinity data is the 1988 "Gas-phase Ion and Neutral Thermochemistry" (the GIANT Tables) (8). This volume is the successor to Rosenstock et al.'s "Energetics of Gaseous Ions" (18) (1977) and Franklin et al.'s "Ionization Potentials, . . ." (19)(1968). The "GIANT" tables include essentially all basicity, acidity, electron affinity, and ionization energy data through 1986, with sporadic coverage since then. They do not include the metal ion relative affinity data of Staley and others (20–30) or

much of the data on solvation and clustering energetics, recently reviewed by Keesee and Castleman (31). In addition, the GIANT tables present the data in order of molecular formula. As a result, the nature of the various equilibrium scales is not readily evident. In the following sections of this review, sources are cited, where available, which present the data in the various scales sorted according to affinity order.

There is also a computer-access (IBM/PC) version of the GIANT tables planned for release in 1989, through NIST.

II. THE SCALES

A. Gas-phase basicities (proton affinities)

This equilibrium scale is probably the most extensively developed of all the current ones, by both low-pressure ICR(32) and high-pressure CIMS techniques (33); the two scales agree quite well (34,35). Commonly referred to as the proton affinity scale (that being the ΔH quantity), the best current available summary of it is the "Evaluated Gas Phase Basicity" publication of Lias, Liebman, and Levin (34) (henceforth LLL). Published in 1984, it is available as a separate offprint from the publisher. It contains listings of proton affinities (ΔH) and basicities (ΔG), in two separate tables, one in affinity order and one sorted according to molecular formula. There have been additional compounds added to the scale since 1984, and these are reported in the GIANT tables (8). As noted, that compilation is sorted only by molecular formula, so it is more difficult to get an overall picture of the basicity scale from it. An updated LLL is being prepared by the original authors for publication in 1989.

The relative basicity scale is well-developed from weak bases such as water (PA = 166.5 kcal/mol) to strong bases like the chelating diamine 1,8-*bis*(dimethylamino)naphthalene (PA = 241.8 kcal/mol), over a 75 kcal/mol range. This region includes most common functional groups and structures. For basicities weaker than that of water, down to methane (PA = 131.6 kcal/mol), LLL includes several partial equilibrium scales anchored to local absolute basicities. In 1985, a complete basicity scale from methane to water was reported (36). That scale, however, seems compressed relative to other absolute basicities (8) by ca. 3 kcal/mol over its 30 kcal/mol span. There is still some uncertainty about the absolute values in this region, although the ordering of the bases is secure. For basicities less than that of methane, only absolute values exist down to that of helium, PA = 42.5 kcal/mol (8).
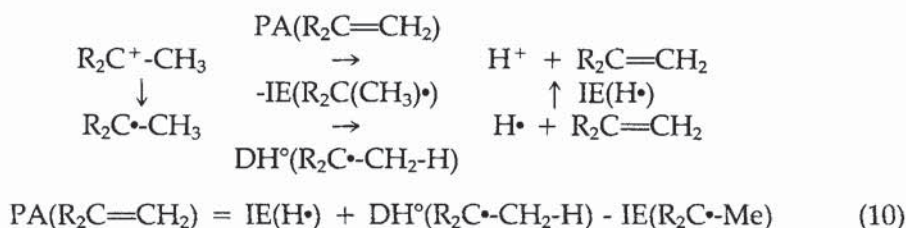
The relative basicity scale is anchored to a number of absolute values known from other threshold experiments and thermochemical cycles. The basicity of water and ammonia are obtained from the photoionization threshold for reactions like:

$$(H_2O)_2 + h\nu \rightarrow H_3O^+ + HO\cdot \tag{9}$$

whereas the PA of ketene is calculated from the appearance energy, and thus the

heat of formation, of CH_3CO^+ which is produced from a number of methyl ketones (37,38).

For the basicity of alkenes such as ethene, propene, and 2-methyl-propene, the thermochemical cycle given in Scheme 1 can be determined

$$PA(R_2C\!\!=\!\!CH_2)$$

$$
\begin{array}{ccc}
R_2C^+\text{-}CH_3 & \rightarrow & H^+ + R_2C\!\!=\!\!CH_2 \\
\downarrow & \text{-IE}(R_2C(CH_3)\bullet) & \uparrow \ IE(H\bullet) \\
R_2C\bullet\text{-}CH_3 & \rightarrow & H\bullet + R_2C\!\!=\!\!CH_2 \\
& DH°(R_2C\bullet\text{-}CH_2\text{-}H) &
\end{array}
$$

$$PA(R_2C\!\!=\!\!CH_2) = IE(H\bullet) + DH°(R_2C\bullet\text{-}CH_2\text{-}H) - IE(R_2C\bullet\text{-}Me) \qquad (10)$$

Scheme 1

from separate experiments (35). The values obtained for the homolytic bond energies and radical ionization energies necessary to evaluate Scheme 1 have varied in the past, such that the absolute values of the basicities reported in various articles must be checked carefully to see what anchor value is being used. This is often denoted by referring the values that are used to the proton affinity of ammonia, in the anchored scale of reference. Ammonia itself is not a very good anchor compound, because there has been considerable uncertainty in its absolute proton affinity; values from 202 to 210 kcal/mol were reported in the literature (34). It is also not especially well-linked to the basicity scale. Nevertheless, because of its central position in the scale, it is commonly quoted as the reference value for a given set of absolute values, even if it is not important in the anchoring scheme itself. The LLL scale has set the proton affinity of ammonia as 204.0 kcal/mol (basicity = 195.6 kcal/mol), and it seems unlikely at present that this will vary much in the future. The scale of gas-phase basicities so obtained for a variety of functional groups is shown in Figure 1.

B. The gas-phase acidity scale

As for the basicity scale, the gas-phase acidity scale was principally established with two different techniques: pulsed CIMS by Kebarle and co-workers (15), and pulsed ICR spectrometry (16). Although these agree quite well at present, there have been problems with their agreement in the past, and with the agreement of the original ICR scale (the 1979 acidity scale) with the absolute anchoring data.

The 1979 gas-phase acidity scale, which was determined by ICR mass spectrometry (16,39,40), was anchored via the thermochemical cycle (41) in Scheme 2 to the value for hydrogen fluoride, an acid in the center of the acidity scale, and one whose absolute acidity from Scheme 2 (often referred to as the "D-EA" cycle) is known to ±0.2 kcal/mol. The absolute acidities for a few other acids in

the scale were similarly available, but not to this accuracy. It was assumed that the relative acidities were otherwise accurate.

$$\Delta H_{acid}(AH)$$

$$AH \quad\quad\quad \rightarrow \quad\quad\quad A^- \quad + \quad H^+$$
$$\downarrow DH°(A\text{-}H) \quad\quad\quad\quad\quad\quad \uparrow \quad -EA(A)$$
$$\rightarrow$$
$$A\bullet + H\bullet \quad\quad IE(H\bullet) \quad\quad A\bullet + \quad H^+$$

$$\Delta H_{acid}(AH) = DH°(A\text{---}H) - EA(A\bullet) + IE(H\bullet) \quad\quad (11)$$
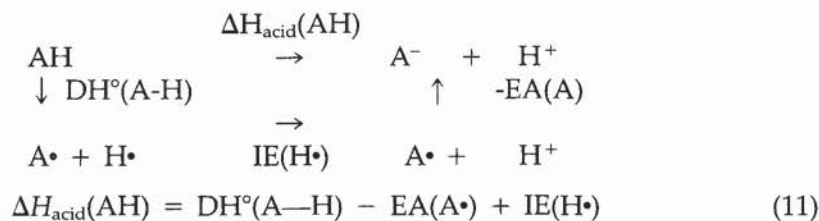
Scheme 2

If the bond strength DH°(A-H) is derived from the gas-phase acidity $\Delta H_{acid}(AH)$ from the 1979 scale, and from the electron affinity EA(A·), by using the converse of Eq. (11), then a DH° (RO-H) of 102 kcal/mol for the various aliphatic alcohols is obtained (16). This is in contrast to the well-established values of 104 ± 1 kcal/mol from kinetic studies in the literature (42). There were other acids in the 1979 scale, such as thiols, whose bond strengths, so derived, also disagreed with literature values, but the uncertainties for the literature DH° values were at that time such that a clear case could not be made for discrepancies with the others (16).
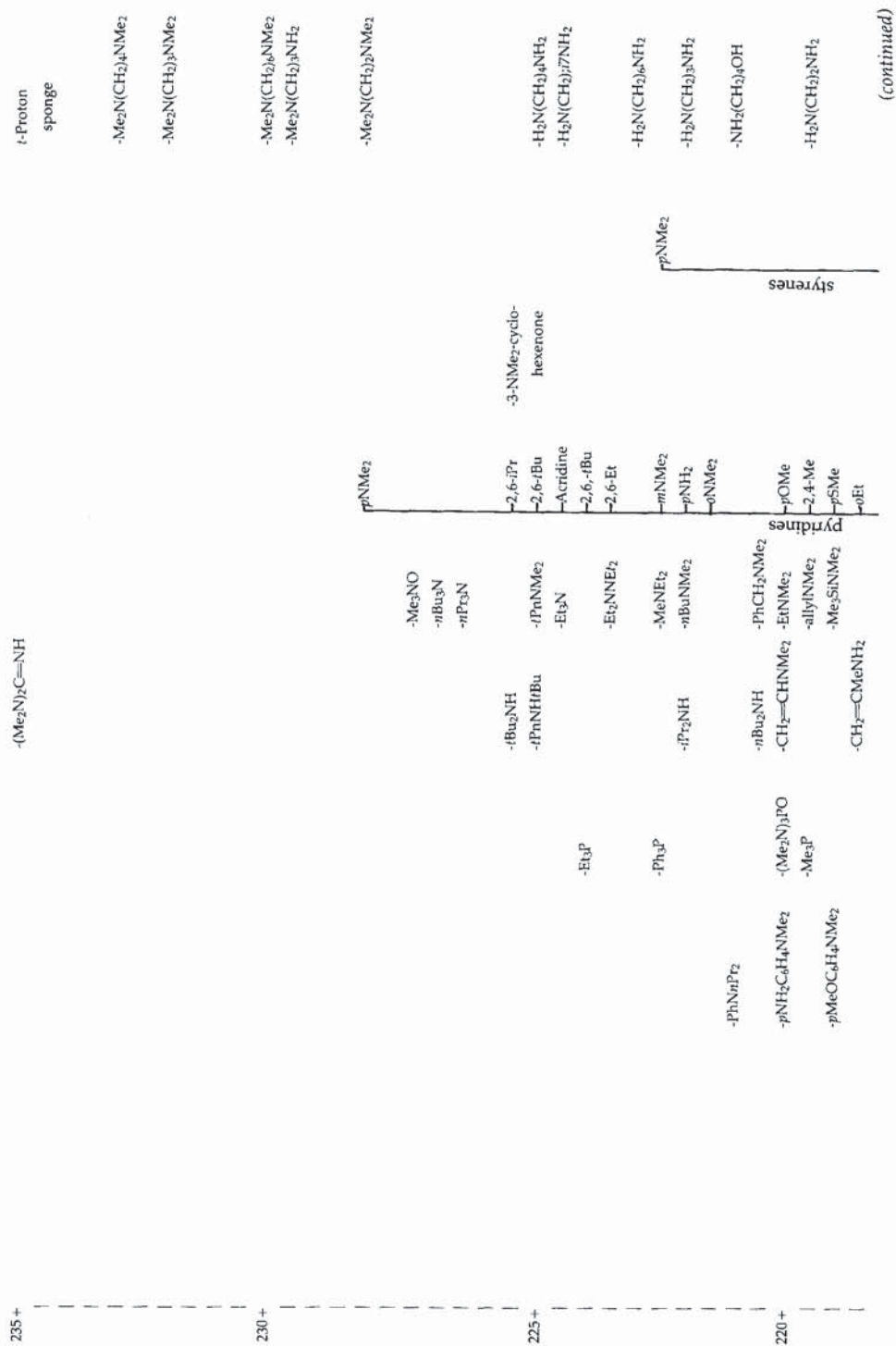
In addition, the 1979 ICR acidity scale has several small discrepancies with the acidity scale that was developed previously by Kebarle and co-workers using a pulsed high-pressure mass spectrometer (15). The high-pressure MS measurements were made at 500K and 600K. These differences were ignored at the time because they were small enough to be due to the large temperature difference between the two sets of data (40).

It was subsequently discovered (16) that the temperatures in ICR cells were somewhat higher than the 300K assumed. This temperature increase is due to heating effects of the rhenium filament that generates the electron beam for ionization. Although modified cell design has obviated this problem for current instrumentation, corrections can be applied to the older data if the filament current is known (16), resulting in an overall average cell temperature of 320K for typical filament currents (43). This expands the relative scales by 7%, but still leaves a considerable discrepancy with the anionic anchoring data.

Recently, two other problems with the data in (16) were found: it now appears that the primary anchor acid, HF, was not accurately measured relative to the rest of the scale (44), presumably because of neutral pressure measurement problems. In addition, Taft and co-workers, in the course of adding many new acids to the scale, discovered a region of bad data in the 1979 acidity scale between t-butyl alcohol and trifluoroethanol. The new data result in an expansion of that region by almost 3 kcal/mol, compared to the 1979 scale.

The resulting relative ICR acidity scale has now been reanchored by the author to 22 absolute acidities derived from Scheme 2 by using the best current data; that resulting anchoring is shown in Figure 2. The slope of the line is 1.019, indicating that the relative ICR acidities from the ladder agree with the absolute

Figure 1. Selected Gas Phase Basicities, ΔG, kcal/mol, from Ref. 8.

235+   230+   225+   220+

- t-Proton sponge
- -Me₂N(CH₂)₄NMe₂
- -Me₂N(CH₂)₃NMe₂
- -Me₂N(CH₂)₆NMe₂
- -Me₂N(CH₂)₃NH₂
- -Me₂N(CH₂)₂NMe₂
- -H₂N(CH₂)₄NH₂
- -H₂N(CH₂)i₇NH₂
- -H₂N(CH₂)₆NH₂
- -H₂N(CH₂)₃NH₂
- -NH₂(CH₂)₄OH
- -H₂N(CH₂)₂NH₂

pNMe₂ — styrenes

- -(Me₂N)₂C=NH

pNMe₂ — pyridines

- -2,6-iPr
- -2,6-tBu
- -Acridine
- -2,6-tEt
- -mNMe₂
- -pNH₂
- -oNMe₂
- -pOMe
- -2,4-Me
- -p5Me
- -oEt

- -3-NMe₂-cyclohexenone

- -Me₃NO
- -nBu₃N
- -nPr₃N
- -iPrNMe₂
- -Et₃N
- -Et₂NNEt₂
- -MeNEt₂
- -nBuNMe₂
- -PhCH₂NMe₂
- -EtNMe₂
- -allylNMe₂
- -Me₃SiNMe₂

- -tBu₂NH
- -iPrNHtBu
- -iPr₂NH
- -nBu₂NH
- -CH₂=CHNMe₂
- -CH₂=CMeNH₂

- -Et₃P
- -Ph₃P

- -PhNnPr₂
- -(Me₂N)₃PO
- -Me₃P
- -pNH₂C₆H₄NMe₂
- -pMeOC₆H₄NMe₂

Figure 1. (Continued)

215+

210+

205+

anilines

pyridines

styrenes

-Me₂Si=CH₂

-Me₂Pb=CH₂
-Et₂Ni

-Mg₂
-FeO

-Ca
-Cp₂Ru

-Sc

-Me₂Sn=CH₂

-Me₃As
-Ti

-CpRh(CO)₂

-Cp₂Fe
-Mn(CO)₅H

-18-Crown-6

-15-Crown-5
-12-Crown-4

-quinodi-
methane

-o-benzyne

-perylene

-EtOCH=CHMe
-cPrC(Me)=CH₂

-pMeC₆H₄NMe₂

-mMeC₆H₄·NMe₂

-pAcC₆H₄NMe₂

-mOMe

-pNH₂
-(Ph)₃N

-oOMe
-pOMe
-pMe

-H

-mI
-mCl

-(Et)₃PO

-P(NMe₂)₃
-P(OMe)₃

-Me₃PO

-(Ph)₃PO

-(Me)₃PO

-(tBu)₂S
-(MeO)₃PO

-Me₂SO

-PhSMe

-Et₂NH
-pyrrolidine
-(allyl)₂NH

-MeCH=NEt

-tPrNH₂
-tBuNH₂
-nOcNH₂
-imidazole
-CH₂=CHNH₂
-iPrNH₂
-F(CH₂)₃NH₂

-PhCH₂NH₂
-EtNH₂
-allylNH₂
-aziridine
-cPrNH₂
-MeCH=NH
-MeNH₂

-HCCCH₂NH₂

-Me₃N

-HC≡CCH₂NMe₂

-Me-aziridine

-Me₂NNH₂

-CCl₃CH₂NMe₂

-CF₃CH₂NMe₂

-NCCH₂NMe₂

-pyrazole

-pSMe
-pMe
-pEt
-mMe
-oNH₂
-pCH=CH₂

-mSMe

-N-oxide

-mOCO₂Me

-2-Cl-6-Me
-pBr
-pCl
-mCOMe

-pCHO
-mCl
-mF

-pCF₃

-oCF₃

-oF
-pCN

-mCN
-pNO₂

-PhCONMe₂
-(Me₂N)₂C=O
-neoPhCONMe₂
-pNMe₂-C₆H₄CO
-tropone
-EtCONHMe

-NMe-pyrrol-
idone

-Me₂NCHO
-Ph₂CO

-MeCOCH=CMe₂

-mNMe₂

-pNH₂

-pOMe

-Me₂NCH₂NMe₂
-NH₂(CH₂)₃OH

-NH₂(CH₂)₆OH

-NH₂(CH₂)₂OH
-MeOCH₂CH₂NH₂

-triglyme

-MeO(CH₂)₄OMe

-diglyme

-2,5-tBu-furan

-MeO(CH₂)₃OMe

-(sBu)₂O

-(iPr)₂S

-CpNiNO
-EtOCH=CH₂
-uridine
-PhC(Me)=CH₂

200 + -CHCl
-Me₆benzene
-MeCOCH₂COMe
-(iPr)₂O

-V
-MeCH=CHCOMe
p-Me
-HO(CH₂)₄OH

-1,6-C₂B₄H₆
-(tBu)₂CO

-CpCr(CO)₃Me
-HCONHMe
-(nBu)₂O

-(PhCH₂)Cr(CO)
-iPrCOMe

-CH₂N₂
-dodecahedrane
-PhCO₂Me
-MeOCH₂CH₂OMe

-acenaphthene
-CF₃CONMe₂

-NH₃
-norborna-
-(nPr)₂CO
-(Me₃Si)₂O

diene
-c-heptanone
-(nPr)₂O

195 + -EtOCOOMe

-Fe(CO)₅
-chrysene
-sym-triazine
-tBuCOMe

-MeCH=CHCH=CH₂
-c-hexanone

-SiH₂
-fluorene
-Et₂CO
-Et₂O

-CpH
-MeCOOEt

-phenanthrene
-(MeO)₂CO
-THF

-Me₂C=CMe₂
-MeCOEt

-1,2-Me-CpH
-c-pentanone

-CH₂NH₂
-HCONH₂
-Me₃SiOH

190 + -cyclopropene
-MeCOOMe
-mBr

-CpCr(CO)₂NO
-Me₂C=CHMe
-CH₂=C=O

-biphenyl
-CH₂=CMeCOOH
-MeOEt

-Ph(CH₂)₄Ph
-HCOOiPr

-V(CO)₆
-Me₂C=CH₂
-CH₂=CMeCHO

-Ph(CH₂)₂Ph
-mCF₃

-o-Xylene
-c-butanone
-1,4-dioxane

-nBuPh
-HCO₂Et
-furan

-CH₂=CHCH=CH₂
-nBuCHO
-(Me)₂O

185 + -iPrPh

-Mn
-EtPh
-EtCOOH
-iPrOH

-CpFe(CO)₂Me
-Cyclobutene
-nPrOH

(continued)

benzaldehydes

p-F, m-Cl, m-CF₃, p-Me, m-OMe, m-Me, m-Cl, p-F, m-F, p-Cl, p-CN, p-NO₂, p-CF₃

-pyrrole
-tBuNC
-MeN=NMe
-MeC₅₂Me
-PhNC
-iPrNC
-H₂NNH₂
-Me₂NCN
-PhNO
-MePH₂
-EtNC
-MeONH₂
-iPrONO
-CF₃CH₂NH₂
-MeNC
-CH₂=NH
-thietane
-(CF₃CH₂)₂NH
-(Me)₂S
-NCCH₂NH₂
-CF₃NMe₂
-EtONO
-PhCN
-MeSSMe
-EtOCH₂CH₂CN
-PhCH₂CN
-nBuCN
-MeNCS
-nPrCN
-CF₃CH₂SEt
-(CF₃)₃CNH₂
-MeONO
-nPrSH
-MeSCN
-EtSH

Figure 1. (Continued)

-HNC
-CH₂=CHCN

-EtCHO

-PhCH₂OH
-EtOH

-MeCN
-PH₃

-HCO₂Me

-MeSH

-MeCHO
-CF₃COSMe
-CF₃CO₂nBu

-CH₂=S

-CF₃CO₂Et

-EtNO₂

-FCO₂Et

-MeNCO

-CH₂ClCOOH

-MeOCH₂CH₂OH
-MeOH

180 + B₄H₈

-PhMe
-cyclohexene
-mBr-toluene

|-Re(CO)₅Me
|-NH₂

-oF-toluene
-oBr-toluene
-MeC≡CMe

|-Me₂Hg
|-Mo(CO)₆
|-B₅H₈
|-W(CO)₆

-pF-toluene
-pCl-toluene

-c-C₅H₈

175 + -Mn(CO)₅Me

-PhF

-MeC≡CH
-1,2,3,4-C₆H₂F₄
-1,2,4,5-C₆H₂F₄

-HN₃

-MeNO₂

-NCCOOEt

-CF₃COOMe
-HCOOH

-Cr(CO)₆

-C₆HF₅
-1,3-butadiyne
-C₆F₆

|-AsH₃

-BrCN

170 + -Ni

-CCl₃CHO

-CCl₃CH₂OH

|-H₂Te

-CH₂F₂

-CCl₃CN
-CH₂(CN)₂
-CS

-MeCOCF₃

-CH₂=CHF

-HNCO

-(CF₃CH₂)₂O

-CF₃CH₂OH

-(CF₃)₂CHOH

-(CF₃)₃COH

(continued)

-CH₂=O

-CF₃COOH

-CF₃CHO

-CF₃COCl

-F₂CO
-CF₃CFO

-HCN

-H₂S

-CF₃NO

-F₃PO
-C₂F₅CN

-PF₃

-H₂NCN

-NCCN

-MeI

-EtCl

-CHF=CHF
-EtF
-HC≡CF

-C₂H₄

165+

-GeH₄

-B₅H₉

160+

-H₂O

-2,4-C₂B₅H₇

155+ -H₂O₂

-S

-Cu

150+

-Zn

-SO₂

-SiH₄

Figure 1. *(Continued)*

-C$_2$H$_2$

-HCO

145+

-NCF

-C$_3$H$_8$

-HI

-CF$_3$I

-I

-(CF$_3$)$_2$CO

140+

-B$_2$H$_6$

-F$_2$SO$_2$

-MeF

-B$_4$H$_{10}$

-C$_2$H$_6$

-NF$_3$

-CHF$_3$

135+

-CO

-NO$_2$

-HBr

-CF$_3$Br

-OF

-CF$_3$Cl

[SO$_3$ = 130, HCl = 129, CH$_4$ = 127]

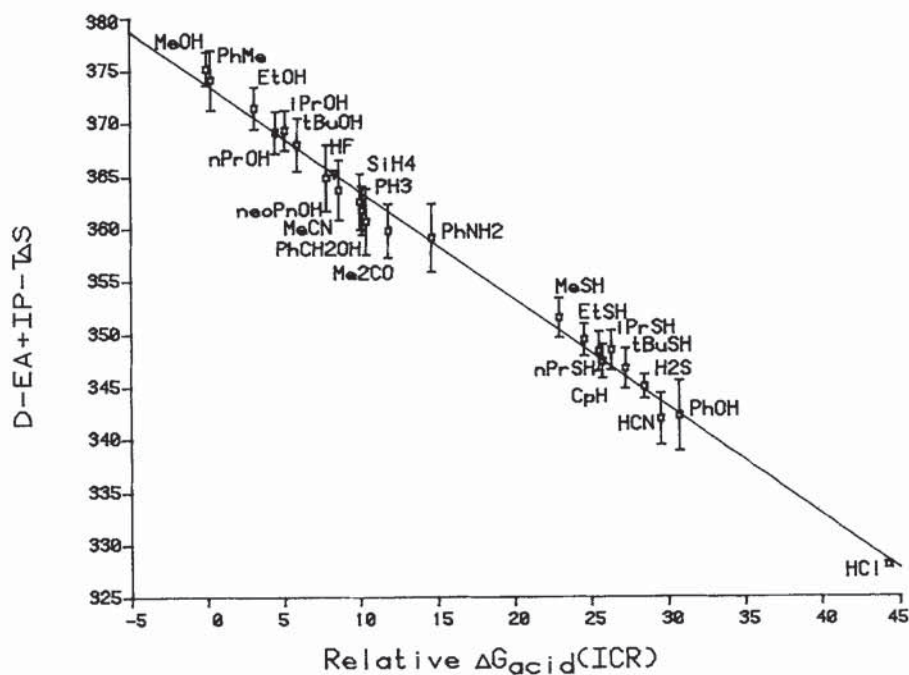**Figure 2.** Relative ΔG_{acid}, ICR, Ref. 8, vs. absolute acidities, Eq. (11), kcal/mol. The line is the least-squares fit to all square points.

values from Scheme 2 to within experimental error over a 45 kcal/mol range. The absolute acidity values that result from these modifications in the 1979 acidity scale, were published in the GIANT tables (8), and are referred to as the "1987 Acidity Scale." The 1987 Acidity Scale includes data from a variety of other sources, especially the pulsed CIMS scale of Kebarle and co-workers (15,45). Agreement is much better than before (40), between the 500–600 K data from pulsed CIMS and the revised 320 K data from ICR experiments, as shown in Figure 3. The two points that noticeably deviate from the unity slope line are Ph_2CH_2 and Me-CONHPh. Their deviation may be due, not to experimental error, but to a much larger change in ΔG_{acid} for the 300–600 K temperature change than that for other acids. Deprotonation of these two acids results in freezing out of a large phenyl group rotor, and the barrier to rotation in the neutral is not known for either Ph_2CH_2 or PhNHCOMe. The temperature dependence of ΔG_{acid}, thus, may be the factor causing this deviation. Likewise, comparison of the difference in acidities of substituted phenols determined by pulsed CIMS (45) and ICR (39) at the 300 K difference in temperatures, as shown in Figure 4, reveals an interesting trend. The non-zero slope for the majority of the phenols indicates that there is an appreciable difference in relative acidities with the change in temperature. This may be attributed to a change in ΔS_{acid} with changing substituent, possibly because of a change in the rotational barrier for the -OH rotor in the acid; this rotor is lost upon ionization. The strong π-donor group p-NH_2 appears to be especially effective for such a rotational change. The acidity scale, with the ranges of common functional groups, is presented in Figure 5.
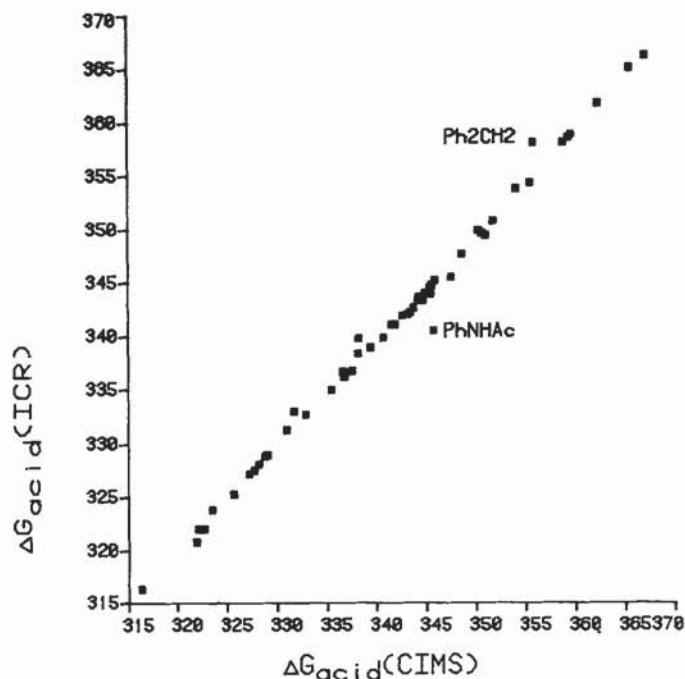
Figure 3. ΔG_{acid} (ICR, 320 K) vs. ΔG_{acid} (CIMS, 500–600 K), kcal/mol. Data from Ref. 8.

C. Electron affinities

Electron affinities have been determined by electron transfer equilibria, and extensive scales of such data have been reported (46). These data are summarized in the GIANT tables (8). Unlike acidities and basicities, however, the bulk of electron affinity data available in the literature does not come from this scale, but rather from direct measurement of absolute electron detachment thresholds [see Eq. (12)].

$$A^- + h\nu \rightarrow A^{\cdot} + e^- \tag{12}$$

where the frequency of the laser (or other monochromatic light source) is varied, and the threshold for the onset of thermal electron detachment is determined (*photodetachment spectroscopy*). An alternate approach is to hold the light frequency constant in excess of that needed to cause electron detachment, and to measure the resulting kinetic energy of the detached electron (*photoelectron spectroscopy*). These techniques were recently reviewed (47,48). These methods, however, operate on a much shorter timescale than do the methods for equilibrium measurements, and thus they produce information about the vertical transition EA_v from the anion to the neutral, not the adiabatic one EA_a. For many anions, such as alkoxides, where the anion geometry is not very different from that of the corresponding neutral, this difference in EA_v and EA_a is quite small, 0.05 eV or
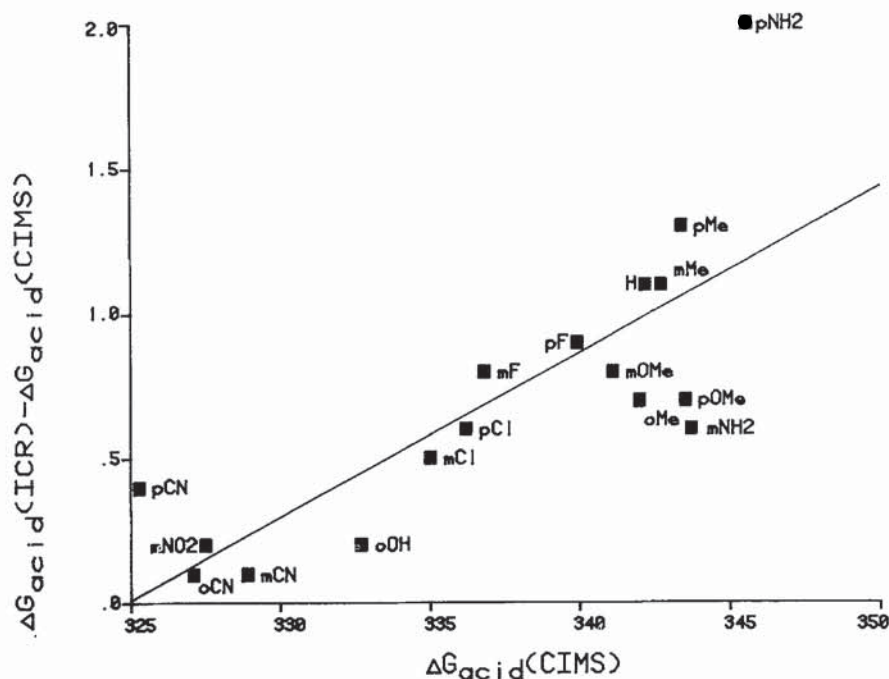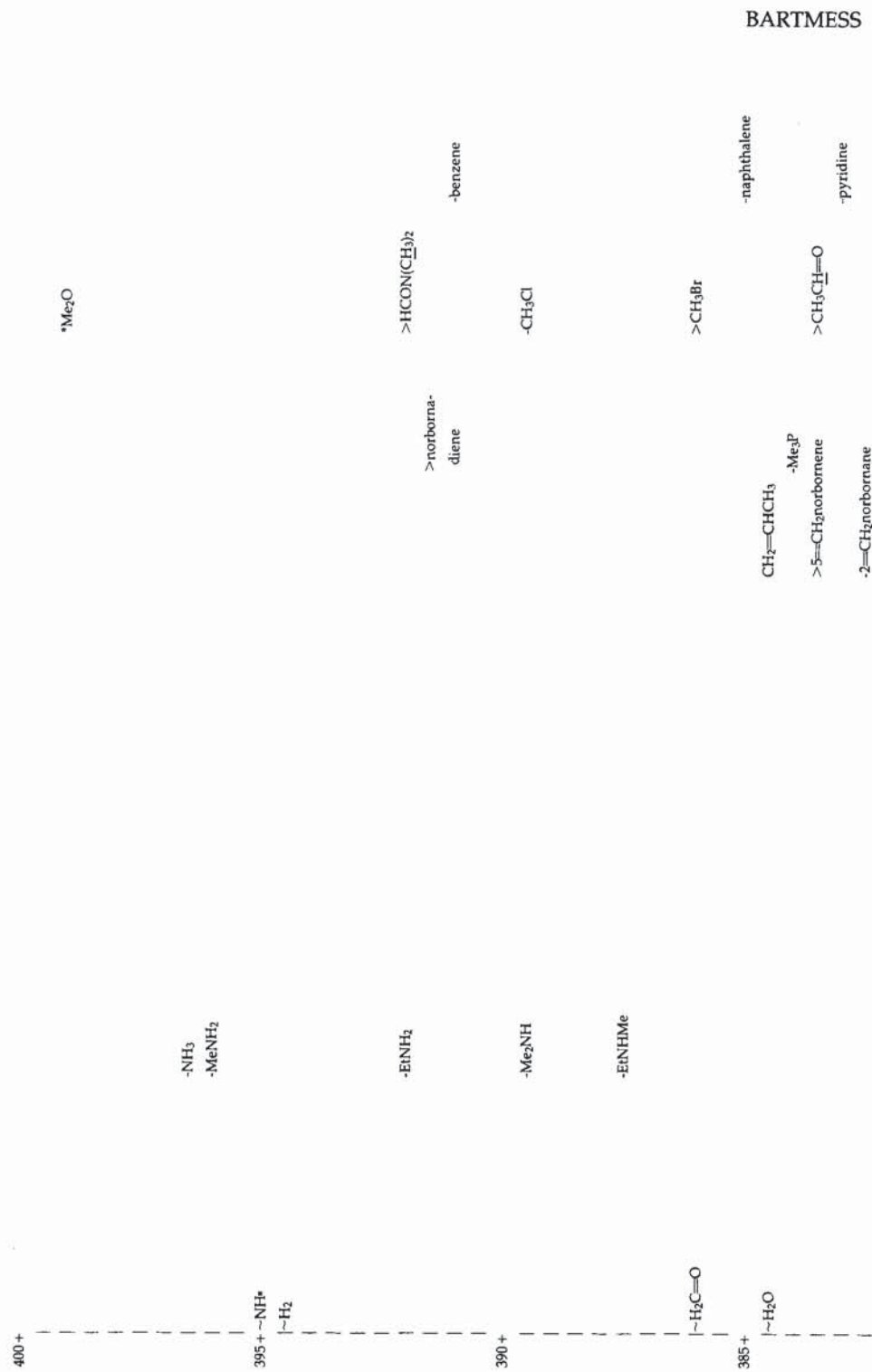
Figure 4. ΔG_{acid} of phenols (CIMS, 600 K) vs. ΔG_{acid} (CIMS) $-$ ΔG_{acid} (ICR), kcal/mol. Data from Ref. 8. The line is the least-squares fit to all the points.

less. For certain structures, such as CF_3, the adiabatic EA can be appreciably less than the vertical EA, ca. 1.0 eV in this case (49). This can be interpreted as a case where the radical is planar but the anion pyramidal. CS_2 is a more subtle case, with the vertical EA 0.4 eV greater than the equilibrium adiabatic EA (46).

Another problem with the electron detachment methods is that the form of the cross-section for the process near threshold is dependent on the structures involved, and the actual thermodynamic onset may have a very gradual increase in cross-section as a function of energy. This is especially true for the aromatic radical anions that make up the bulk of the equilibrium scale (50). The compounds that tend to give the sharper onsets in electron detachment are the closed shell species, such as alkoxides, that are not as amenable to the equilibrium electron transfer technique (however, see Ref. 51). One last difference is that the electron detachment threshold methods yield 0K values for the EA, an enthalpic quantity, because onset is at the 0-0 transition. If the vibrational frequencies for the neutral and anion are known, the value for the EA can be corrected to 298 K.

The equilibrium method gives the relative ΔG for electron transfer at some non-zero temperature. The ΔH for electron transfer can be obtained by measuring the equilibria as a function of temperature, via the van't Hoff method (46). This again yields only the relative entropies of electron transfer, but they are anchored to the absolute value for SO_2 calculated by using statistical mechanics (46). The exact values for these entropies are dependent on the entropy of the electron, which

Figure 5. Selected gas phase acidities, ΔG, kcal/mol, $-$ = Equilibrium method; $>$ = bracketing; $\sim$ = D$-$EA$+$IP cycle; $*$ = branching ratio.

400 +

395 + $-$NH$\cdot$
    | $\sim$H$_2$

390 +

385 +

$-$NH$_3$
$-$MeNH$_2$

$-$EtNH$_2$

$-$Me$_2$NH

$-$EtNHMe

| $\sim$H$_2$C=O

| $\sim$H$_2$O

$*$Me$_2$O

>norborna-
diene

>HCON(CH$_3$)$_2$

$-$benzene

$-$CH$_3$Cl

CH$_2$=CHCH$_3$
            $-$Me$_3$P
>5=CH$_2$norbornene
$-$2=CH$_2$norbornane

>CH$_3$Br

>CH$_3$CH=O

$-$naphthalene

$-$pyridine

(continued)

- quinoline
- pyrimidine
- -PhSCH₃
- -Me₂N-N=O
- -MeCONMe₂
- -EtCN
- -HCSNMe₂
- >mF-C₆H₃OMe
- -CF₃H
- -CPrCN
- -1,3-dithiane
- -MeSOMe
- -MeCO₂Me
- -MeCN
- -MeOCH₂CN
- ~MeCOEt
- >CH₂=SiMe₂
- >CH₂=CFMe
- >CH₂=C(CHO)Me
- ~cycloheptatriene
- -CH₂=C(CF₃)Me
- -CH₂=CHCN
- -CH₂=C(CN)Me

toluenes:
- pMe
- -H
- -PhEt
- -PhiPr
- -pF
- -mF
- -mCONMe₂
- -pCl
- -mCHO

- -MeC≡CH
- -nPrC≡CH
- -tBuC≡CH
- -HC≡CH
- -PhC≡CH

- -MeOH
- -EtOH
- -nPrOH
- -iPrOH
- -tBuOH
- -cHxCH₂OH
- -MeOCH₂CH₂OH
- -tBuCH₂OH
- *nOcOH
- *tHpOH
- -tBuCH(Me)OH
- -Et₂NOH
- -PhCH₂OH
- ~(CH₂=CH)₂CH₂

380+ |~CH₂
      |~HO•
375+ |-HOOH
370+ |~HF
365+ >PhN•
      |-SiH₄
      |-PH₃

Figure 5. *(Continued)*

Scale markers and entries (gas-phase acidity scale, rotated):

360+

355+

350+

345+

toluenes

anilines

-PH•
-CH•
-HNO
>AsH₃
-HOCl
-LiH
-BH
-GeH₄
-SiH
-HOO•
-HS
-H₂S + H₂S
-HCN

-tBuCH(iPr)OH
-t(Bu)₂CHOH
-Me₂C=NOH
-MeCH=NOH
>(FCH₂)₂CHOH
-tBuCH=NOH
-CF₃CH₂OH
-CF₃CH(Me)OH
-CF₃C(Me)₂OH
-MeSH
-EtSH
-nPrSH
-iPrSH
-tBuSH
-sBuSH
-PhCH=NOH
-tBuCH₂SH

-H₂NCONH₂
-Me₂NCOC≡CH
-HCONHMe
-HCONH₂
-NF₂H
-tBuCONH₂
-pyrrole
-3Me-pyrazole
-PhCONH₂
-pyrazole
-H₂NCOCO₂Et
-pCN-PhC≡CH

ClCH₂C≡CH

-MeCOCCH
-MeO2CCCH

-CF₃CCH

-pCOCF₃

-mCN
-mCF₃
-mNO
-pCF₃
-pSOMe
-pCONMe₂
-Ph₂CH₂
-mNO₂
-pCO₂Me
-pCOMe
-3,5-diCF₃
-pCN
-pCOPh
-pCHO
-pSO₂Me
-mCF₃PhCH₂Ph
-mCNPhCH₂Ph
-pNO

pMe
mMe
-H
-PhNHMe
-oF
-mSMe
-2,4-diF
-pCl
-mCOMe
-mCl
-1,5-NH₂-naphthalene
-mSCF₃
-mCN
-pCO₂Me
-mNO₂
-1,8-NH₂-naphthalene

-PhNHEt
-Me₅CpH
-MeNO₂
-EtNO₂
-tBuCH₂NO₂
-pNH₂
-pNMe₂
-NH₂

H₂C=C=O
-CpH
-indene
-9-tBu

-FCH₂CN
-PhSO₂CH₂Me
-PhSO₂nPr
-PhSO₂Me
-PhSO₂-cPr
>CHCl₃
pNMe₂
pMe
-PhCH₂CN
-mF

-MeCOMe
-tBuCOMe
-MeCOiPr
-(iPr)₂CO
-MeCHO
-4,4-Me-cyclo-hexenone
-CH₂=CHCOCH₃
-tBuCH₂CHO
-PhCOCH₃
-PhCOEt
>MeCOCH₂F
-cyclohexenone
>MeCFO
-MeCH=CHCH=O
-PhCH₂COMe

(continued)

>(FCH₂)₂CO → $>(FCH_2)_2CO$
-CF₃COCH₃ → $-CF_3COCH_3$
-CF₃SO₂Me → $-CF_3SO_2Me$
-CH₃COCN → $-CH_3COCN$
-(MeCO)₂CH₂ → $-(MeCO)_2CH_2$
-CF₃SO₂CH=CHMe → $-CF_3SO_2CH=CHMe$
>F₂CHCOCHF₂ → $>F_2CHCOCHF_2$
-PhCOCH₂COMe → $-PhCOCH_2COMe$
-dimedone
>CF₃COCF₂H → $>CF_3COCF_2H$
-barbiturate

ArCH₂CN
pF, pCl, mCl, mCF_3, pCF_3, mCN, mNO_2, $CH_3(CN)_2$, pCN

fluorenes
9-Et, 9-iBu, 9-tBuCH₂, 9-Ph, 1,4-Ph-CpH, 1,3-Ph-indene, triPh-indene, fluoradene

phenols
pOH, mMe, $miPr$, $ptBu$, $mOMe$, mOH, oF, $otBu$, oCl, mF, pCl, $mCOMe$, mCl, $mSOMe$, $mCHO$, oOH, mCF_3, $pSOMe$, pCF_3, mSO_2Me, $pCOMe$, $pSCF_3$, oCN, $pCHO$, $pCOPh$, pCN

anilines
$pCHO$, pCN, $3,5-diCF_3$, pSO_2Me, mSO_2CF_3, pNO_2, pSO_2CF_3, mSF_5, pSF_5

benzoic acids
pSO_2CF_3, $pCOCN$, pNH_2, mNH_2, pMe, mMe, H, $mOMe$, oMe, mOH, pF, pOH, $pCOMe$, mCl, $pCHO$, mCF_3

bicyclo[2.2.2]octylCO₂H
-H, 4-Me, 4-OMe, 3-CL, 4-F, 3-CN, 4-Br, 4-CN, 4-NO₂

-imidazole
-indole
-H₂NCONHCOMe → $-H_2NCONHCOMe$
-MeCONHPh
-indazole
-(MeCO)₂NH → $-(MeCO)_2NH$
-succinimide
-carbazole
-CF₃CONH₂ → $-CF_3CONH_2$
-Cl₃CCONH₂ → $-Cl_3CCONH_2$
-MeCONH₂ → $-MeCONH_2$
-benztriazole
-CF₃CONHPh → $-CF_3CONHPh$

-MeCO₂H → $-MeCO_2H$
-(CF₃)₂CMeOH → $-(CF_3)_2CMeOH$
-EtCO₂H → $-EtCO_2H$
-iBuCO₂H → $-iBuCO_2H$
-tBuCH₂CO₂H → $-tBuCH_2CO_2H$
-tBuCO₂H → $-tBuCO_2H$
-1-Ad-CO₂H → $-1-Ad-CO_2H$
-3ClnPrCO₂H → $-3ClnPrCO_2H$
-PhCH₂CO₂H → $-PhCH_2CO_2H$
-Cl(CH₂)₂CO₂H → $-Cl(CH_2)_2CO_2H$
-EtCHClCO₂H → $-EtCHClCO_2H$
-MeCHClCO₂H → $-MeCHClCO_2H$
-MeCHBrCO₂H → $-MeCHBrCO_2H$
-ClCH₂CO₂H → $-ClCH_2CO_2H$
-CF₃CH₂CO₂H → $-CF_3CH_2CO_2H$
-BrCH₂CO₂H → $-BrCH_2CO_2H$

~NaH
~KH
340+
~HSiF₃ → $~HSiF_3$
335+
>FeH
330+
~HCl
325+

Figure 5. (*Continued*)

is not a well-defined quantity (8). In some cases, the ΔS terms can be appreciable: the entropy of electron attachment for most nitroaromatics is 0 to -5 eu, but $+10$ eu for hexafluorobenzene and $+13$ eu for SF_6. These values are consistent with reasonable geometry changes on electron attachment: the rotation of the nitro group is frozen out on electron attachment to nitro-substituted aromatic compounds, but loss of the symmetrical structure and loosening of bonds in $SF_6^{-\cdot}$ causes an increase in entropy (52).

Thus, the two methods are often complementary for the types of structures with which they can deal. The equilibrium scale can be anchored with the electron detachment thresholds, corrected to 298 K (46). Combining the values from the threshold methods and the equilibrium scale, a scale of electron affinities can be set up over a 100 kcal/mol range, although the threshold values above ~ 4 eV are rather sparse and not confirmed by the equilibrium method so far.

There are also extensive EA data for values less than 0.5 eV from the electron capture detector (8,53), where the absolute EA is determined from the ratio of attachment and detachment rate constants. Although some of these on the more bound end of the range agree with equilibrium and photodetachment values, most of them have not been verified by an independent method. These are the only values available in this range at present, however. Figure 6 shows the electron affinity for typical structures from all of these methods.

D. Organic cation affinities

The bond strength between an ion and a neutral can be determined in the gas phase via "solvent switching" reactions:

$$B_1H^+\cdot\cdot B_2 + B_3 \rightleftarrows B_1H^+\cdot\cdot B_3 + B_2 \tag{13}$$
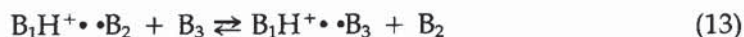
to yield the relative bond strengths. Such data have been primarily determined by direct equilibrium methods (see below) although some data were obtained by use of the drift-cell ICR at relatively high pressures (36). More recently, temperature-dependent equilibria in pulsed CI have been used to examine clustering equilibria where direct equilibrium methods fail. The failure is due to reaction of the ionic species with its own vapor (54). The data are discussed below, in Section II.I. There are also equilibrium data for switching of more exotic ions, such as Me_2B^+ (55).

For some ions, such as CH_3^+, one can construct an ion affinity scale based on proton affinities of the proper methylated compounds. Because:
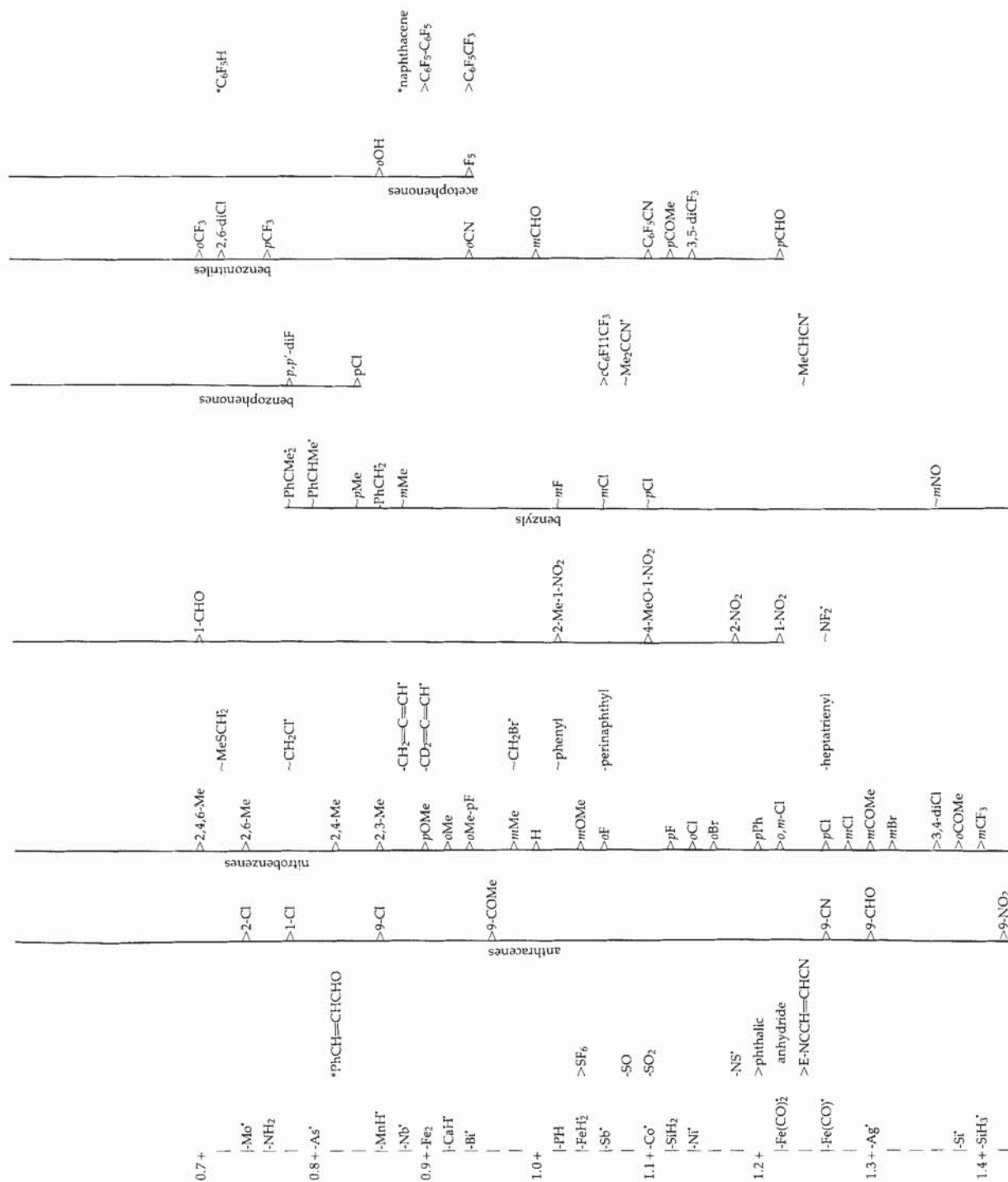
$$\Delta H_f (Me_2OH^+) = PA(Me_2O) - \Delta H_f (H^+) + \Delta H_f (Me_2O) \tag{14}$$

then the "methyl cation affinity" of methanol can be calculated to be:

$$MCA(MeOH) = \Delta H_f (CH_3^+) + \Delta H_f (MeOH) - \Delta H_f (Me_2OH^+) \tag{15}$$

Limited scales of this type can be constructed, as given in Table I. Figure 7 shows

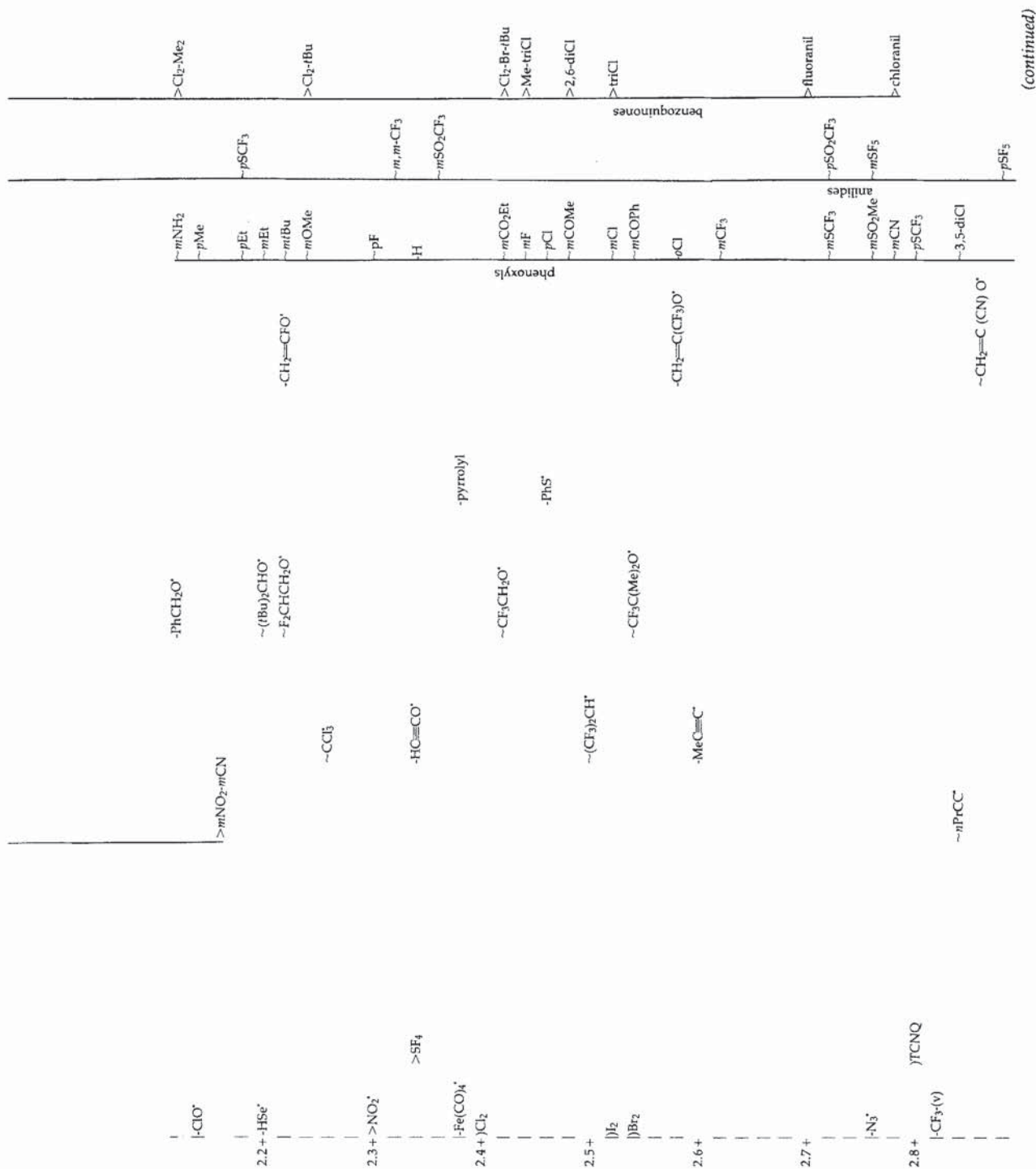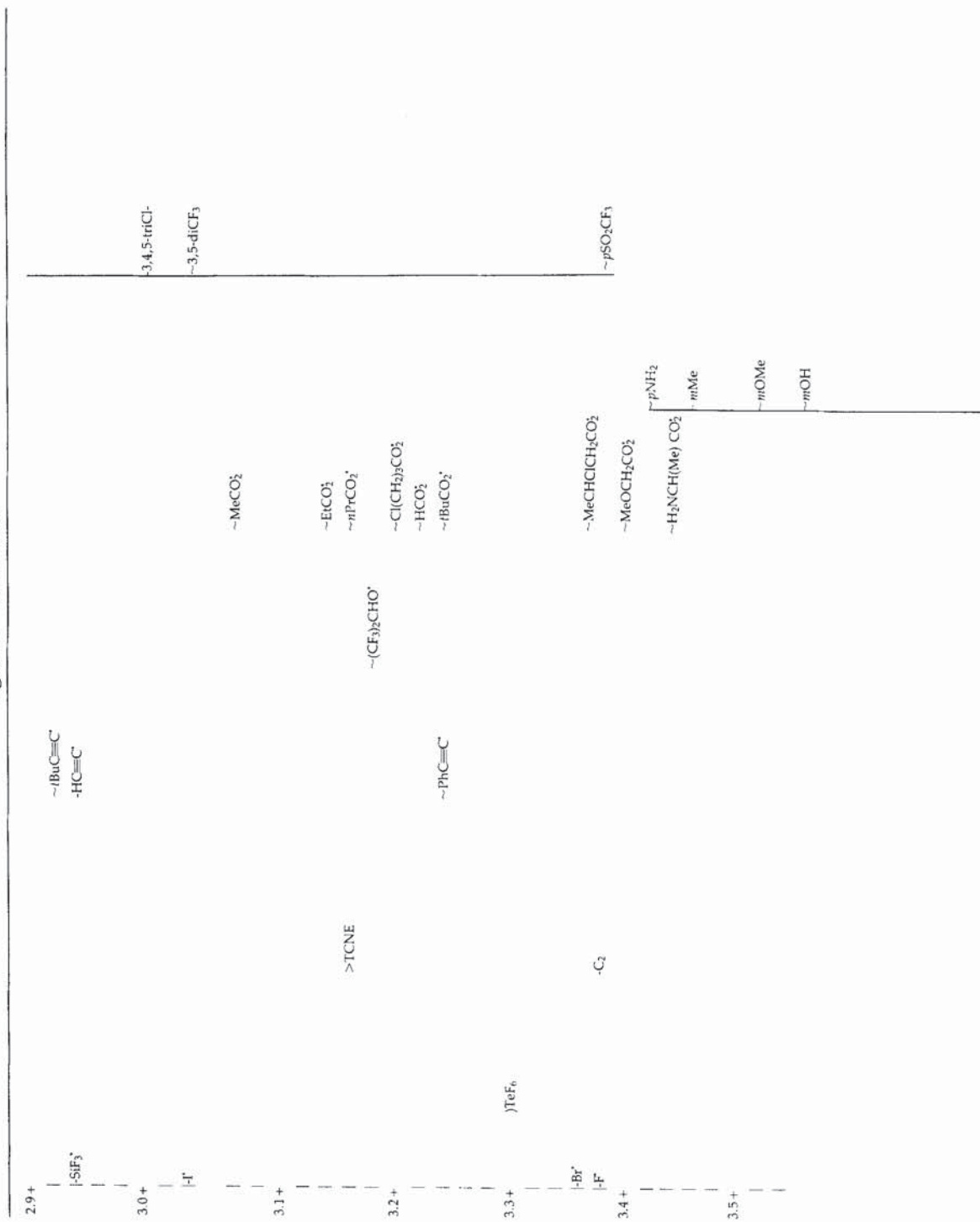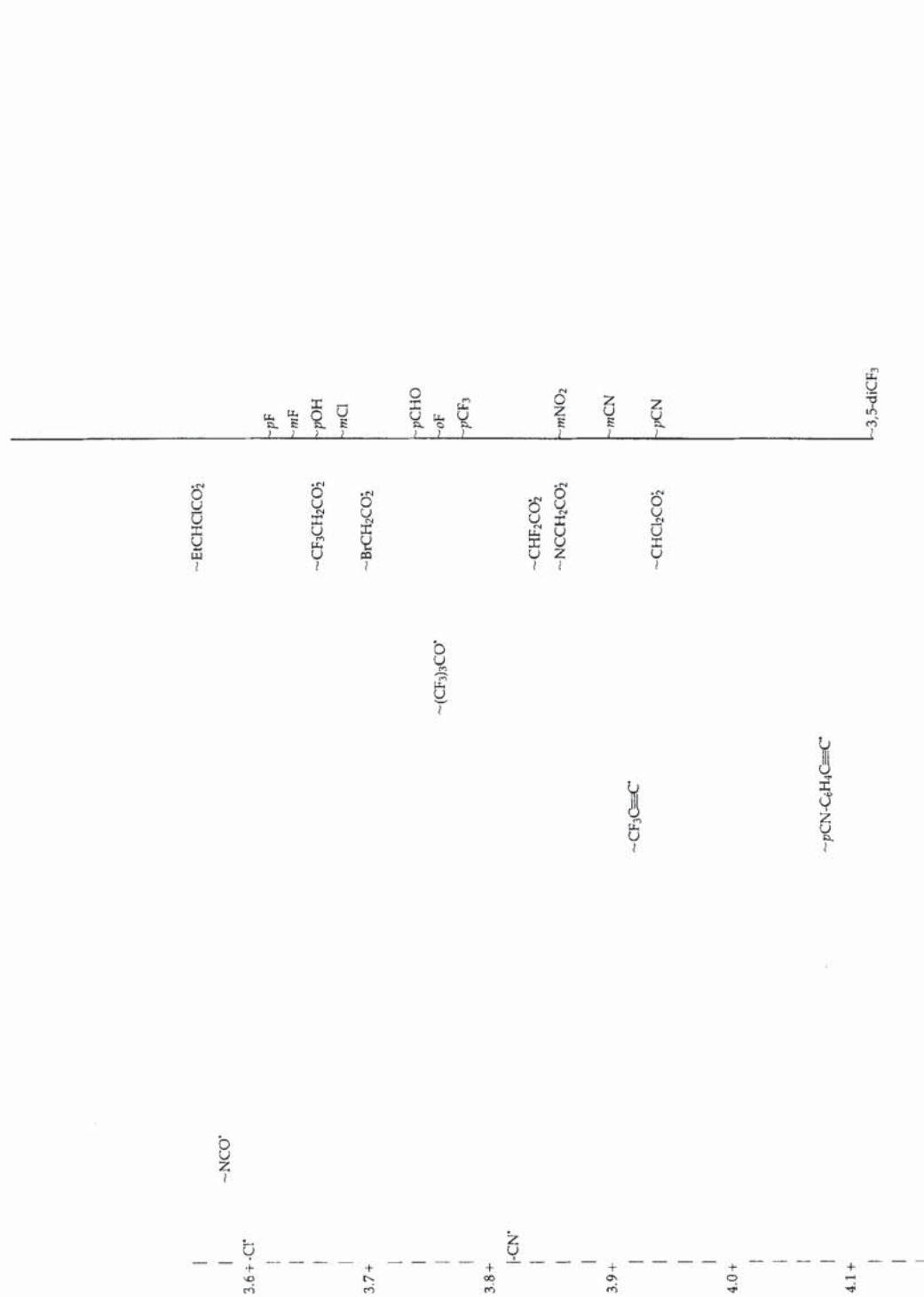**Figure 6.** Selected electron affinities, eV, from Ref. 8. − = ±0.1 abs., ±0.01 relative; ~ = ±0.2 abs.; * = ± unknown (Electron Capture Detector).

*1,2,4,5-Me benzene
*o-Cl$_2$
*1,2,3,5-Me benzene
*Me$_6$benzene
*Ph$_2$CH$_2$
*indene
*Me$_5$benzene

*fluorene
*triphenylene
*phenanthrene
*PhCCPh
*1,3,5-Cl-benzene
*PhCH=CHPh
*acenaphthylene

*1,2,4,5-Cl-benzene

*azulene
*benz[e]pyrene
*diEt phthalate
-o-benzyne
*dibenz [a,j]
*benz[a] anthracene
*benz[a]pyrene

*H
*PhCOEt
pF
oF
*2,4,6-Me
pCl
mCl
oCF$_3$
mCF$_3$

H
mCF$_3$
OCF$_3$

*PhCO$_2$Me
*2,3,5,6-F$_4$anisole

>C$_6$F$_6$
*C$_6$F$_5$OMe

H
pF

~Me$_2$N
~Et(Me)N
~MeNH

~EtNH

*H
2-Me
1-Me
2-Et
*1,4-Me
*1-Cl

naphthalenes

*oCO$_2$Me
*1-COMe
*2-CHO
>2-CN
*1-CN

-HCO

-CH$_2$=CHCH$_2$

~C$_7$H$_7$

pMe
mMe
*H
*2,4,6-Me
pF
*p-CHO
*oF
*mF

benzaldehydes

H

anthracenes

-CS
*N$_2$O
-HNO
*COS
-O$_2$
-H$_2$C=C:
>CS$_2$
*COT
*CS$_2$
-CH$_2$
>MeCOCOMe

-Ti
-Fe
-Sc
0.2 + -Tl
-B
0.3 + -In
-Ta
-Pb
-NH
-Zr
-Al
-Cs
-NiH
0.5 + -K
-V
-Et$_2$NO
-C$_4$H
-P$_2$
0.6 + -Li
-Co

0.0 +

0.1 +

0.4 +

·C₆F₅H

·naphthacene
>C₆F₅-C₆F₅
>C₆F₅CF₃

▷oOH

acetophenones

△F₅

>oCF₃
>2,6-diCl
▷pCF₃

benzonitriles

▷oCN

△mCHO

>C₆F₅CN
▷pCOMe
>3,5-diCF₃

▷pCHO

>p,p'-diF

▷pCl

benzophenones

>cC₆F11CF₃
~Me₂CCN·

~MeCHCN·

~PhCMe₂·
~PhCHMe·

▷pMe
PhCH₂
~pMe

benzyls

~mF

~mCl

~pCl

~mNO·

△1-CHO

△2-Me-1-NO₂

△4-MeO-1-NO₂

△2-NO₂
△1-NO₂

~NF₂·

~MeSCH₂·

~CH₂Cl·

·CH₂=C=CH·
·CD₂=C=CH·

~CH₂Br·

~phenyl

·perinaphthyl

·heptatrienyl

△2,4,6-Me
△2,6-Me

△2,4-Me

△2,3-Me

△pOMe
△oMe
△oMe-pF

△mMe
△H

△mOMe
△oF

△pF
△oCl
△oBr

△pPh
△o,m-Cl

△pCl
△mCl
△mCOMe
△mBr

△3,4-diCl
△oCOMe
>mCF₃

nitrobenzenes

△2-Cl

△1-Cl

△9-Cl

△9-COMe

anthracenes

△9-CN

△9-CHO

△9-NO₂

·PhCH=CHCHO

>SF₆

-SO
-SO₂

-NS·
>phthalic
anhydride
>E-NCCH=CHCN

0.7+

|-Mo·
|-NH₂

0.8+ -As·

|-MnH·
|-Nb·
0.9+ -Fe₂
|-CaH·
|-Bi·

1.0+

|-PH
|-FeH₂
|-Sb·

1.1+ -Co·
|-SiH₂
|-Ni·

1.2+

|-Fe(CO)₂⁺
|-Fe(CO)·

1.3+ -Ag·

|-Si·
1.4+ -SiH₃·

|-CoH₂·

>maleic anhyd.

Figure 6 (*Continued*)

benzoquinones: anthraquinone, >triMe, >n-benzo quinone, >2,6-diMeO, >2,5-diMe, >2,6-diMe, >naphthoquinone, >Me, >2,3-MeO-5-Me, >2,6-tBu, >H, >2-Cl-3,6-diMe, >2-Ph, >2-Ph, >2-Cl-5-tBu

anilides: pMe, mMe, PhNMe·, PhNEt·, >H, mCO₂Me, mCOMe, ·F, mSCF₃, mCN, mSO₂Me

>pCN-F₄

~Me₂C=C(Me)O·, ·C₇ enolate, ·CH₂CN·, -2-norbornanone, ·C₈ enolate, ·EtCH=CHO·, ·MeCH=C(Et)O·, ·EtCH=C(nPr)O·, ·CH₂=C(Et)O·, ·CH₂=C(OMe)O·, ·tBuCH=CHO·, ·CH₂=C(tBu)O·, ·C12 enolate, ·CH₂=C(iPh)O·, ·PhCH=CHO·

>3,5-diCF₃, ·MeS·, ·EtS·, ·nPrS·, ·iPrS·, ~iBuS·, ~tBuCH₂S·

·MeO·, ·CD₃CD₂O·, ·EtO·, ~nBuO·, ·iPrO·, ·iBuO·, ·tBuO·, ·tBuCH₂O·, ·sBuO·, ~tBuCH(Me)O·, ~tBuCH(Et)O·

~Ph₂CH, ·1-Me-Cp·, ·Cp·, ~C₂F₅, ~CF₃·, ~fluorenyl, ~indenyl

nitrobenzenes: >pCF₃, >oCHO, >pCOMe, >mCN, >oCN, >mNO₂, >pCHO, >pCN, >3,5-diCF₃, >pNO₂

anthracenes: >1,5-diNO₂, >1,3-diNO₂

·O·, ·FeO·, ·PhN, ·Ir·, ·GeH₃·, ·S₂, ·TeO, +Fe(CO)₃·, ·HO·, ·SeO₂, ·CCO, ·EtN, ·NiH₂·, ·Te₂·, ·Se₂, ·Te·, ·Se·, ·S·, ·S₃·, +TeH·, ·Pt·

1.5+, 1.6+, 1.7+, 1.8+, 1.9+, 2.0+, 2.1+

benzoquinones

>Cl₂-Me₂ · >Cl₂-tBu · >Cl₂-Br-tBu · >Me-triCl · >2,6-diCl · >triCl · >fluoranil · >chloranil

$$>Cl_2\text{-}Me_2 \quad >Cl_2\text{-}tBu \quad >Cl_2\text{-}Br\text{-}tBu \quad >Me\text{-}triCl \quad >2,6\text{-}diCl \quad >triCl \quad >fluoranil \quad >chloranil$$

anilides

$pSCF_3$ · $m,m\text{-}CF_3$ · mSO_2CF_3 · pSO_2CF_3 · mSF_5 · pSF_5

phenoxyls

mNH_2 · pMe · pEt · mEt · $mtBu$ · $mOMe$ · pF · H · mCO_2Et · mF · pCl · $mCOMe$ · mCl · $mCOPh$ · oCl · mCF_3 · $mSCF_3$ · mSO_2Me · mCN · $pSCF_3$ · $3,5\text{-}diCl$

Other species:

- $-CH_2=CFO^\bullet$
- $-CH_2=C(CF_3)O^\bullet$
- $\sim CH_2=C\,(CN)\,O^\bullet$
- -pyrrolyl
- $-PhS^\bullet$
- $-PhCH_2O^\bullet$
- $\sim(tBu)_2CHO^\bullet$
- $\sim F_2CHCH_2O^\bullet$
- $\sim CF_3CH_2O^\bullet$
- $\sim CF_3C(Me)_2O^\bullet$
- $\sim CCl_3$
- $-HC\equiv CO^\bullet$
- $\sim(CF_3)_2CH^\bullet$
- $-MeC\equiv C^\bullet$
- $>mNO_2\text{-}mCN$
- $\sim nPrCC$

Affinity scale (eV):

value	species
	$-ClO^\bullet$
2.2 +	$-HSe^\bullet$
2.3 +	$>NO_2^\bullet$
	$>SF_4$
	$-Fe(CO)_4^\bullet$
2.4 +	$)Cl_2$
2.5 +	$)I_2$; $)Br_2$
2.6 +	
2.7 +	$-N_3^\bullet$
2.8 +	$)TCNQ$; $-CF_3(v)$

(continued)

Figure 6 *(Continued)*

~NCO·

3.6+ -Cl·

~EtCHClCO$_2^-$

~pF
~mF
~pOH
~mCl

3.7+

~CF$_3$CH$_2$CO$_2^-$

~BrCH$_2$CO$_2^-$

~(CF$_3$)$_3$CO·

~pCHO
~oF
~pCF$_3$

3.8+ -CN·

~CHF$_2$CO$_2^-$
~NCCH$_2$CO$_2^-$
~mNO$_2$

3.9+

~CF$_3$C≡C·

~mCN

~CHCl$_2$CO$_2^-$
~pCN

4.0+

~pCN-C$_6$H$_4$C≡C·

4.1+

~3,5-diCF$_3$

Table I. Selected methyl cation affinities and proton affinities.

Base	MCA[a]	PA[b]	A$^-$	MCA[c]	$\Delta H_{acid}(AH)$[b]
Me$_2$PH	133.3	216.3	CH$_3^-$	314.7	416.6
MePH$_2$	123.3	204.1	H$^-$	313.9	400.4
Me$_2$NH	121.9	220.6	CH$_2$=CH$^-$	309.3	406.0
EtNH$_2$	118.0	217.0	C$_6$H$_5^-$	304.1	400.7
MeNH$_2$	114.8	214.1	NH$_2^-$	293.7	403.6
PhNH$_2$	114.1	209.5	Me$_3$Si$^-$	293.5	381.2
PH$_3$	104.6	188.6	CH$_2$=CHCH$_2^-$	291.3	390.8
NH$_3$	104.3	204.0	MeC≡C$^-$	286.6	381.1
MeSH	99.8	187.4	CF$_3^-$	285.5	377.0
MeNC	97.3	171.0	O$^{-\cdot}$	283.4	382.2
Me$_2$CO	95.4	196.7	PhCH$_2^-$	281.4	380.8
PhOH	89.3	196.3	HO$^-$	276.7	390.7
MeCHO	87.7	186.6	PhC≡C$^-$	275.5	370.7
MeC≡N	84.3	190.0	NO$^-$	275.5	363.1
H$_2$S	83.4	170.2	CH$_2$CN$^-$	274.2	372.9
MeOH	83.1	181.9	MeO$^-$	272.0	380.6
HCO$_2$Me	79.3	188.4	PH$_2^-$	271.8	370.9
CO	78.9	142.0	CH$_2$=C(Me)O$^-$	270.4	369.1
CH$_2$=O	78.3	171.7	PhSO$_2$CH$_2^-$	264.7	362.7
HI	69.6	147.1	tBuO$^-$	263.3	374.6
H$_2$O	67.5	166.5	PhNH$^-$	262.8	366.4
MeCl	64.7	163.0	CCl$_3^-$	262.3	357.1
HBr	61.3	139.0	CN$^-$	261.1	351.2
HCl	56.2	128.6	F$^-$	260.9	371.4
MeF	55.3	145.0	PhCH$_2$O$^-$	259.6	370.0
PhH	53.5	181.3	CH$_2$=NO2$^-$	258.5	356.4
Xe	51.3	118.6	MeN=CHO$^-$	256.8	360.4
N$_2$	45.3	118.2	MeS$^-$	256.0	356.9
HF	34.2	117.0	tBuS$^-$	250.9	352.5
NO$_2$	33.2	140.0	CF$_3$CH$_2$O$^-$	248.2	361.8
			HS$^-$	247.4	351.2
			MeCO$_2^-$	238.9	348.6
			PhO$^-$	238.0	349.2
			NO$_2^-$	234.7	339.6
			Cl$^-$	226.5	333.4
			Br$^-$	219.5	323.5
			I$^-$	212.6	314.4
			CF$_3$CO$_2^-$	208.1	322.8

[a]From Eq. (15), ca. ± 3 kcal/mol.
[b]Ref. 8.
[c]MCA(A$^-$) = $\Delta H_f(CH_3^+) + \Delta H_f(A^-) - \Delta H_f(ACH_3)$, ca. ± 3 kcal/mol. Data from Refs. 8 and 181.

that such Lewis basicities do not always parallel proton affinities; on the basis of proton affinities, third row atoms bond to the methyl cation more strongly than do second row atoms.

E. Metal cation affinities

The use of metal ions has been proposed as a method of selectively ionizing a variety of analytes, with considerable control in structural selectivity (56). Metal ions can be generated in mass spectrometers by either electron ionization of

Figure 7. Methyl cation affinities vs. proton affinities; Data from Table I. The line is the least-squares fit to the amine and alcohols points, and has slope 0.985 ± 0.031.

suitable volatile precursors, such as metal carbonyls (57,58), or by direct laser volatilization of metal surfaces (59–63). Such methods can be implemented without too much difficulty on most mass spectrometers, so that this technique may be used considerably more widely in the future. There has been a considerable body of data obtained in regard to the reactivity of various metal ions with a wide variety of functional groups (58,64). Scales of relative attachment affinities of metal ions to these compounds have been determined (20–30), but at present most of these scales have not been anchored to absolute values. Data for Cu^+ (23,29), Mn^+ (25), Al^+ (24,26), Ni^+ (28), Li^+ (20,21), Mg^+ (24), $FeBr^+$ (27), and $CpNi^+$ (22,30) are available.

F. Hydride and chloride ion affinities

Equilibrium (16) can be established with Y = H (65–67) or Cl (68–70),

$$R_1^+ + R_2Y \rightleftarrows R_2^+ + R_1Y \tag{16}$$

to obtain relative cation stabilities. Hydride abstraction reactions of this type are important in CIMS, especially when CH_3^+, $C_2H_5^+$ (65,66), and NO^+ are used as reagent ions (67). Chloride transfer equilibria are also used for determination of relative cation stabilities (68,70). A good summary of this topic is in Ref. 5, and

extensive tables of hydride ion affinities (HIA) are given in Ref. 35. Most of the data in the latter do not come from measurement of reaction (16), but by calculation from:

$$HIA(R^+) = IE(R\cdot) + DH°(R-H) - EA(H\cdot) \qquad (17)$$

On the basis of these calculated HIAs, hydride transfer from alkyl structures to NO^+, a common reagent for this type of reaction, should be endothermic for primary C-H, thermoneutral for secondary C-H, and exothermic only for tertiary C-H and Si-H, and C-H α to an amino group, a phenyl group, or doubly allylic. Table II contains hydride ion affinities for selected cations.

G. Anion affinities

The relative attachment energies for fluoride (71–73), chloride (71,72,74–77), cyanide (78,79), alkoxides (80,81), and other anions (31) to a wide variety of species have been determined by the equilibrium methods. The fluoride scale is the most extensively developed for both hydrogen-bonding acids and Lewis acids. Many of these studies were done at constant temperature, and the entropy for the process was estimated by statistical mechanics (17). The entropies estimated in this way are probably not as accurate as those for acidities, because for acidities a strong covalent bond with accurately known geometry and frequencies is lost. For anion affinities, the loss is typically of a much looser hydrogen bond. Unfortunately, we know little of the bond length and much less the vibrational frequencies, of such hydrogen bonds. These scales have been anchored to absolute affinities obtained from the direct equilibrium method (see below).

There is also an extensive scale of halide affinities of transition metal halides, developed by the technique of Knudsen-cell MS (82–101). This work, principally from the groups of L.N. Sidorov and A.V. Pyatenko, involves both equilibrium halide transfer (variable temperature, 800–1150 K) as well as direct equilibrium measurements. These in general are species in which the halide is bonded to the neutral species much more strongly than halide is to the organic and nontransitional metal species examined by ICR. The ICR scale for fluoride affinities extends up to ~85 kcal/mol ($PF_5 \cdot \cdot F^-$), whereas the lowest fluoride affinity from the Knudsen cell work is 81 kcal/mol. At present, there are no confirming data for these Knudsen cell values from a second technique. See Table III for a selection of fluoride affinity values.

H. Ionization energies

Ionization energies (IE) are most commonly obtained from direct ionization threshold measurements (electron ionization or photoionization), or appearance energies of fragment ions, plus the necessary auxiliary neutral thermochemistry (8). These methods, however, yield the vertical IE, and as such are not applicable to cases where the geometries of the ion and neutral are appreciably different. An example of this is alkyl hydrazines, for which the neutral species tends to adopt a lone-pair–gauche conformation, and the radical cation becomes conju-

gated (eclipsed) for electronic reasons. The equilibrium electron transfer method provides accurate adiabatic IEs in this case, anchored to known absolute IEs that do not involve large geometry changes (102).

Such IEs (or for the reverse process, the recombination energies) are useful for interpreting the amount of fragmentation occurring in the analyte, based on the exothermicity of charge transfer. The IEs have been shown to correlate with the amount of reagent ion adduct formation versus simple charge transfer for a series of analytes (103).

I. Direct equilibrium affinity measurements

Gas-phase basicities (3) and acidities (4), being in the 40–400 kcal/mol range, cannot be measured directly with current instrumentation. The kinetics in the endergonic direction for equilibria of that magnitude are such that the ions would have to be trapped for more than 10^{28} collisions with the neutral gas in order to attain equilibrium, even for the smallest value of 40 kcal/mol. With pulsed CIMS, ion abundances can be examined out to ~2×10^5 collisions at best, whereas the ICR and flowing afterglow are in the 10^3–10^4 collision range.

For cation and anion affinities such as shown by the reactions in Eqs. (6) and (7), and involving attachment of metal ions or simple hydrogen bonding, the values of ΔG are often in the range of 5–20 kcal/mol. In such cases, it is possible to set up and measure the equilibrium "half-reaction" (18) directly by utilizing CIMS. This technique requires the high pressure of CIMS to be successful.

$$MB^+ \rightleftharpoons M^+ + B \tag{18}$$

Because the net reaction is an exothermic addition as written, the excess energy of reaction remains in the product, and this energy must somehow be lost or the product ion will simply fragment back to reactants. The unimolecular lifetime for such excited species must be comparable to the collision time with the bath gas, in order for "termomolecular" collisions to remove the excess energy effectively and stabilize the addition product. If neutral gas pressures are sufficiently high in the ICR spectrometer to cause such collisional stabilization, then the collisional broadening of the ICR signal interferes with proper detection of the ion.

In addition, entropy favors the experimentalist in such reactions, because the increase in translational entropy makes ΔS (18) positive, typically $+15$ to $+30$ eu (31). This results in ΔH (18) values up to ~30 kcal/mol being accessible by this technique.

Such CIMS experiments have been performed for stepwise solvation energetics of cations and anions (14). These data are also commonly used as the absolute anchoring values for the corresponding scales of relative affinities (35,71,78,80). The available data were recently comprehensively reviewed (31,104,105). To summarize a large body of data, symmetric proton bound dimers of the form $BH^+ \cdots B$ have an intrinsic bond strength based on the electronegativity and hydridization state of the atoms involved in the hydrogen bond, with -OH$^+ \cdots$ O- >

-NH$^+$ $\cdot\cdot$ N > -SH$^+$ $\cdot\cdot$ S-, etc. The bond strength stays roughly constant if sub-stituents on the two hydrogen bonded atoms are varied in a symmetric way: as one becomes a better donor, the other becomes an equally worse acceptor, thus maintaining the hydrogen bond strength at a relative constant value. If only one partner is changed, the bond strength changes about 30–50% of the change in gas-phase basicity or acidity, depending on the exact functional group involved (105,106). Typical values are 23 kcal/mol for ΔH for symmetric amine proton-bound dimers, 32 kcal/mol for alcohol and ether dimers, and 30 kcal/mol for Me$_2$C=OH$^+$ $\cdot\cdot$ O=CMe$_2$. Et$_2$O $\cdot\cdot$ $^+$H$_3$NMe is bound by 22 kcal/mol, and even ethylene is bound to ammonium by 10 kcal/mol (31).

Hydrogen bonding, although it strengthens the bond, is not necessary: Me$_4$N$^+$ is bound to Me$_3$N by 10 kcal/mol, and even a base as weak as methane will bind to NH$_4^+$ by 3.6 kcal/mol (31). Chelation, as with α,ω-diamines, results in even stronger bonding, but at an entropic price of 5–15 eu (104).

III. NONEQUILIBRIUM CONSIDERATIONS

A. Kinetics

As noted above, reactions that exceed more than a few kcal/mol endergonic usually are not observed in CIMS, because of the limited trapping time of the instrumentation. In general, only exergonic reaction processes are observed, al-though a few exceptions are known, because of an ion's internal energy-driving process. There are several special cases where a simple prediction based on this "all exergonic/no endergonic reactions" rule may not be valid. Neutral analytes are commonly present as 0.1% to 1% of the reagent gas concentration. There is a mass law effect, therefore, favoring the reaction of an ion with the CI reagent gas, relative to that ion reacting with the neutral analyte. Conversely, if a reagent ion is the conjugate base or acid of the reagent gas, such as NH$_4^+$ in NH$_3$, HO$^-$ in H$_2$O, etc., the presence of the reagent gas in $\sim$1000-fold excess over the analyte shifts the proton transfer equilibrium away from the desired (M + H)$^+$ or (M − H)$^-$ of the analyte. At 200°C, the result is an apparent additional 6 kcal/mol endero-gonicity in the proton transfer reaction. Reactions which are exergonic within the 0–6 kcal/mol range may not yield appreciable amounts of analyte ions, therefore.

Many exothermic ion/molecule reactions proceed at or near the collision rate, because the strong interaction between the ion and the neutral results in a complex that is typically 8–30 kcal/mol more stable than the reactants. If there is some barrier to reaction, it is situated at the bottom of the potential well, resulting in an effective reduction of the barrier. It is not uncommon for ion/molecule reactions to have negative temperature dependence or no temperature dependence at all, implying that the potential barrier is actually below the energy of the reactants. Some ion/molecule reactions, however, were shown to proceed much slower than the collision rate (107). Although this subject has not been widely investigated, the majority of reactions that involve transfer of a proton from one localized lone pair to another localized lone pair usually proceed at essentially the collision rate, with an abrupt dropoff of the probability of a reactive collision for reactions which

are within 2–4 kcal/mol of thermoneutral (108). In contrast, those species for which the Lewis/Brønsted base has a delocalized electron pair to which the ion is starting to bond, often react more slowly than expected, especially when the energetics are near to thermoneutrality. Examples of this reduction in reactivity include alkenes as neutral bases (109), and enolates, nitronates, benzyl anions, etc. as anionic bases (107). Steric hindrance can also reduce the rate of such reactions (110). The reactions can be driven at near-collision rates, however, if they are 10 kcal/mol or more exothermic (110).

As a result of such slow reactions, equilibrium is not always attained in CIMS, even for reactions that are near-thermoneutral (111). Quantitative conclusions cannot be drawn about equilibrium constants from ion intensities without additional proof that equilibrium was achieved. Use of pulsed CIMS (112) is usually necessary to show that ion ratios are constant with time.

Although enthalpy is a commonly used criterion for the feasibility of a reaction in CIMS, it was shown that there are "entropy-driven reactions" (113). These occur when the observed process is rapid, in spite of being endothermic, because the entropy of the process makes it exergonic. The true criteria for reactivity, thus, should be free energy; the bias toward enthalpy as the determining factor in ion/molecule reactivity is probably due to the availability of such data from threshold measurements and to a lack of corresponding free energy data, from the period before equilibrium data generally were available (114).

B. Temperature

Temperature becomes a factor in CIMS when entropy is important in determining product ratios. Higher temperatures favor dissociation of adduct ions into the ion and neutral molecule (115–117). There are more subtle effects seen in the equilibrium scales: when enthalpy changes are derived from measured free energy changes, using entropy values calculated from statistical mechanics, a change in apparent ΔH over several hundred degrees can be attributed to a non-zero heat capacity change for the process, as noted above for the gas-phase acidity scale. This is a factor of 1 to 2 kcal/mol, however, for compounds that do not involve internal hydrogen bonds. Chelation (cyclization) of an ion can result in changes in free energy of more than 5 kcal/mol over the room temperature to 300°C range (104).

C. Other problems

Other problems that result in reactivities that appear to be contrary to the scales presented here include neutral–neutral reactions and wall reactions. The former typically involve reaction of neutral analytes with free radicals such as H• and R• present in the source, followed by ionization by the reagent ions (118). For example, $(M + 3H)^+$ ions from ammonia CI of α,β-unsaturated carbonyls and nitriles are observed (119,120). Tetracyanobenzoquinone was used as a free radical trap in a test for such reactions (121). Reactions of the radical anions of polycyclic aromatic hydrocarbon with oxygen adsorbed on the walls was also observed (122).

Table II. Selected hydride ion affinities of cations and neutrals

Cation	HIA[a]	Neutral	HIA[b]	Neutral	HIA[b]
$Me_2N=CH_2^+$	198	CO	6	O_2	57
$PhCH_3^{-\cdot}$	201	$nPnSiH_3$	11	$CH_2=CHCOMe$	58
$MeNH=CH_2^+$	205	$HC\equiv N$	12	CF_3COMe	62
$Me_2C=OMe^+$	209	H_2O	17	$CH_2=C=O$ (at CO)	63
$CH_2NH_2^+$	216	benzene	21	SO_2	63
$Me_2C=OH^+$	217	$AsH\cdot$	22	quinodimethane	63
$PhCMe_2^+$	220	SiH_4	22	$Me_2Si=CH_2$	63
$MeCH=OMe^+$	220	NH_3	24	$CF_3CH=O$	63
$C_6H_6^{+\cdot}$	221	$CH_2=NH$	35	$HC\equiv CC\equiv N$	69
Me_3Si^+	223	$CH_3C\equiv CH$	35	$PhSO_2CH=CH_2$	71
$MeCO^+$	223	$HC\equiv CH$	36	p-benzoquinone	84
tBu^+	233	$CH_2=C=O$ (at CO)	37	$(CF_3)_2C=O$	86
$MeOCH_2^+$	236	$Me_2C=O$	38	o-benzoquinone	97
$PhCH_2^+$	237	$MeCH=O$	39	I_2	105
NO^+	246	$NO\cdot$	40	Br_2	122
iPr^+	250	$EtCH=O$	40	$O\cdot$	127
MeS^+	255	$Et_2C=O$	41	$C\equiv N\cdot$	130
CH_2OH^+	255	$CH_2=O$	42	Cl_2	135
$allyl^+$	256	$(iPr)_2C=O$	43	$C\equiv C\cdot$	168
$PhNH^{+\cdot}$	261	$tBuCOMe$	44	$HC\equiv C\cdot$	169
H_3Si^+	262	$PhCH=O$	46	F_2	198
$PhO^{+\cdot}$	266	$tBuCH=O$	46		
Et^+	271	$PhCH=CH_2$	49		
CH_2F^+	291	$CH_2=S$	49		
I^+	295	$(tBu)_2C=O$	49		
$CH_2C\equiv N^+$	307	$CH_2=C(CN)Me$	50		
CH_3^+	315	$CH_2=C=CH_2$	50		
Br^+	343	CO_2	52		
Cl^+	385	$CH_2=CHCOnPr$	53		
OH^+	402	$CH_2=CHC\equiv N$	57		

[a]Hydride ion affinity, from Eq. (17), kcal/mol, ca. ± 4 kcal/mol.
[b]HIA $= \Delta H_f(H^-) + \Delta H_f(A) - \Delta H_f(AH^-)$, kcal/mol. Data from Ref. 8, ca. ± 4 kcal/mol.

IV. APPLICATIONS

A. Negative chemical ionization

Negative ions can be generated for analysis either by ion/molecule reaction with other anions or by electron attachment of thermalized electrons. These areas were recently reviewed (6,123). For the former case, the majority of the data deal either with gas-phase acidities or with anion attachment to the analyte via a solvation-type reaction.

The common reagent ions for proton abstraction and solvation, and their sources, include NH_2^- (NH_3), $HO^-(N_2O/CH_4)$, $O^{-\cdot}(N_2O/N_2)$, $MeO^-(MeONO/CH_4)$, F^- (CF_4 or NF_3), and Cl^- (a variety of chlorinated organics, typically CCl_4). As shown in Figure 5, amide (NH_2^-) is the strongest Brønsted base that can currently be generated in good yield by electron ionization. Amide will deprotonate *all* organic compounds with a hydrogen to give an $(M - H)^-$ ion, save alkanes, ethers, and tertiary amines. These latter two classes are liable to react, but principally to give E_2-type elimination products. Amide is thus not selective. For the more acidic

Table III. Fluoride affinities of neutrals[a]

A	DH(A-F⁻) Ref.	A	DH(A-F⁻) Ref.	A	DH(A-F⁻) Ref.
AlF_3	116.6 (99)	Et_3B	51.0 (71)	$tBuOH$	33.3 (17)
ScF_3	112.3 (99)	$MeSiF_3$	50.5 (71)	$iPrOH$	32.3 (17)
Be_2F_4	111.0 (93)	$(CF_3)_2CO$	49.7 (71)	$nPrOH$	32.3 (17)
GaF_3	110.3 (96)	AsF_3	48.2 (71)	$nBuOH$	32.2 (17)
FeF_3	107.8 (100)	F_3PO	47.9 (71)	COS	31.8 (71)
CoF_3	105.4 (101)	Me_3B	47.2 (71)	CO_2	31.7 (71)
ThF_4	104.2 (91)	CF_3CF_2CFO	47.2 (71)	EtOH	31.5 (17)
MnF_2	102.7 (88)	FCOCOF	45.7 (71)	CS_2	31.3 (17)
HfF_4	102.5 (99)	$CF_3CF{=}O$	45.6 (71)	$PhNH_2$	31.2 (17)
UF_4	102.1 (99)	HCO_2H	45.3 (17)	$CF_3CF_2CF_2C{\equiv}N$	30.8 (71)
MoF_5	101.9 (95)	$MeCO_2H$	44.1 (17)	C_2F_5H	30.4 (17)
AuF_3	101.8 (97)	$(EtO)_3B$	44.0 (71)	$CF_3CF_2C{\equiv}N$	30.1 (17)
UF_5	101.4 (86)	SF_4	43.8 (17)	Me_4Si	29.9 (71)
MnF_3	100.6 (92)	SO_2	43.8 (17)	MeOH	29.6 (17)
UF_3	99.3 (94)	$CF_2{=}O$	42.6 (17)	$CF_3C{\equiv}N$	29.2 (71)
ZrF_4	99.3 (90)	$(MeO)_3B$	42.0 (71)	$CF_3CH_2NH_2$	28.1 (17)
BeF_2	97.3 (93)	PhOH	41.3 (17)	CF_3H	27.1 (17)
$MoOF_3$	96.2 (95)	$Fe(CO)_5$	40.9 (178)	$CF_2{=}CH_2$	26.7 (179)
RhF_3	95.8 (92)	PF_3	40.2 (17)	CF_2HCH_2F	26.5 (17)
MoF_4	91.8 (95)	$HC{\equiv}N$	39.5 (17)	$F_2C{=}CFH$	26.3 (17)
FeF_2	85.8 (100)	CF_3CH_2OH	39.1 (17)	$(CF_3)_2C(Me)OH$	26.0 (17)
PF_5	85.0 (71)	FH	38.6 (17)	$(CF_3)_2CHOH$	25.0 (17)
CuF_2	83.8 (98)	Me_3SiF	38.2 (71)	$tBuCHO$	24.6 (17)
NiF_2	80.8 (99)	$(FCH_2)_2CHOH$	37.8 (17)	$PhCH_2F$	24.4 (17)
BF_3	78.9 (94)	F_2SO	37.4 (17)	HOH	23.3 (14)
SO_3	78.0 (71)	$(CHF_2)_2O$	36.0 (17)	$tBuF$	22.3 (17)
BF_3	72.0 (71)	SO_2F_2	35.8 (17)	$(CH_3)_3COH$	17.0 (17)
SiF_4	60.0 (71)	$CH_2{=}C{=}O$	35.3 (17)	$MeC{\equiv}N$	16.0 (72)
Et_2BF	58.0 (71)	FCH_2CH_2OH	34.8 (17)	$CHF{=}CH_2$	15.6 (179)
UF_6	56.6 (94)	HSH	34.6 (17)	$CH_2{=}C{=}CH_2$	15.0 (17)
KF	53.5 (87)	MeSH	34.2 (17)	Xe	6.5 (180)
$(MeO)_2BF$	52.0 (71)	pyrrole	34.2 (17)	$CH_2{=}CH_2$	6.0 (179)

[a]ca. ±0.3 kcal/mol relative, ±2.5 kcal/mol absolute, for Refs. 17, 71; ca. ±3 to 8 kcal/mol for Refs. 86–101.

functional groups such as carboxylic acids, the exothermicity of the proton transfer can leave sufficient internal energy in the product ion so that further decomposition occurs. Examples of the reactions are successive eliminations (124) or decarboxylation (125). Amide can deprotonate compounds to give what appear to be unstabilized carbanions, but these carbanions are really stabilized via dipole interactions through space (126). Ammonia is good at thermalizing electrons (7), so that electron attachment ions can also occur when this reagent gas is employed, especially for analysis of species without acidic protons. Because of adventitious water in the vacuum system, hydroxide is a frequent companion ion with this reagent gas. Hydroxide arises from the 12 kcal/mol exothermic proton transfer from water to amide.

The exothermicity of proton transfer with NH_2^- as the base often causes further fragmentation and unexpected reactions. With a series of phenols, $(M - 2)^-$ ions were observed for a number of these, along with prominent amounts of the expected ArO⁻ and ArO⁻ · · HOAr anions (127). These are especially abundant

for p-methyl and p-hydroxy phenoxides and could arise by loss of a hydrogen atom from the para-substituent of the phenoxide to yield quinoid-type radical anions. Such reactions are near-thermoneutral if amide is the base (8). It is also possible that electrophilic aromatic substitution is occurring:

$$ArOH + NH_2^- \rightarrow ArNH^- + H_2O \qquad (19)$$
$$\underset{(M)}{} \qquad \underset{(M-2)^-}{}$$

In low-pressure CI, such as in the ICR spectrometer, water is often used as a reagent gas for production of hydroxide. The actual process involves primary production of hydride ion from water, followed by fast proton transfer with the reagent gas to give hydroxide (128). At the higher pressures used in conventional CIMS, however, water is difficult to pump away cleanly and rapidly. The result is considerable termolecular adduct formation to give $HO^- (H_2O)_n$ ions. These latter species complicate the spectra considerably, because of solvent transfers to the analyte ions. The cluster ions also interfere with the thermochemical selectivity of the reagent ion, because the successive solvation makes the various $HO^-(H_2O)_n$ ions decrease in basicity with increasing n (129). Hydroxide is thus typically generated via the sequence:

$$N_2O + e^- \rightarrow O^{-\bullet} + N_2 \qquad (20)$$

$$O^{-\bullet} + CH_4 \rightarrow CH_3^- + HO^- \qquad (21)$$

avoiding the presence of water in the reagent gas (130).

From Figure 5, it is seen that hydroxide will deprotonate most organic functional groups, including all hydroxy groups, but it is somewhat selective for amines. Simple aliphatic primary and second amines are not sufficiently acidic to be deprotonated by hydroxide, but amines such as $CF_3CH_2NH_2$, $PhNH_2$, and $(Me_3Si)_2NH$, with anion-stabilizing substituents, yield $(M - H)^-$ ions. It appears that the acidity of diisopropylamine is very close to that of water (131). Hydroxide can also remove a proton from certain aromatic rings if strongly electron accepting groups such as $-CF_3$, $-CN$, and -halo are present (132). Allylic and diallylic structures are also deprotonated by hydroxide (133). Effects of excess energy are seen in some proton transfers to hydroxide; for example, 1,2-diols are especially prone to give $(M - 3H)^-$ ions, as well as the expected $(M - H)^-$ ion (134). The latter presumably arises from H_2 loss α,β to the acidic hydroxy group, to give an enolate ion. The extra stability from the intramolecular hydrogen bond may provide the necessary driving force for this elimination; unfortunately, the acidity that is needed to evaluate the exothermicity, that of an α-hydroxy ketone, is not available.

The atomic oxygen anion, $O^{-\bullet}$, is less basic than hydroxide, but it will abstract almost any available hydrogen atom from an analyte or reagent gas mixture to give hydroxide (135). If N_2O is used with N_2 as the diluent reagent gas, then $O^{-\bullet}$ is observed to react with aromatic rings in a nucleophilic substitution reaction, apparently to give phenoxides (135,136). This reaction is 33 kcal/mol exothermic for benzene, and more so for most substituted aromatics. Thus, it will always be

thermochemically viable. $O^{-\cdot}$ also can abstract H_2 to give water plus radical anions corresponding to $(M - 2H)^{-\cdot}$ (136–138). This can happen with a weak acid such as ethene, where proton transfer to $O^{-\cdot}$ is ~21 kcal/mol endothermic.

Methoxide (139) will deprotonate all -OH groups other than those on water. Methoxide will also deprotonate carbon acids if the CH site is directly attached to a cyano, nitro, carbonyl, sulfoxide, sulfone, or phenyl group. It will not deprotonate simple allylic structures, although doubly allylic structures are sufficiently acidic. It will not deprotonate CH groups α to simple sulfides. Elimination is a possible alternate reaction pathway. This reaction can occur even with leaving groups as weak as alkoxides, from elimination in ethers (140).

Fluoride (141) is more selective than the more basic anions (142). It has been used as a carboxylic-specific reagent (143) in coal samples, although it will deprotonate many alcohols and carbon acids as well. It is especially prone to form adduct ions with hydrogen bond donors (142), including the smaller alcohols (17), and to give both $(M - H)^-$ and $(M + F)^-$ with diols (115,144). Like methoxide, fluoride also can cause E2 eliminations in substrates capable of such reactions, even with leaving groups as poor as alkoxides (140).

The radical anion of molecular oxygen, $O_2^{-\cdot}$, is easily generated by electron attachment to molecular oxygen (139). It is commonly present in atmospheric pressure ionization spectra (145). Thermochemically, this ion should deprotonate all carboxylic acids and phenols, although in practice it appears to be nonreactive with the weaker phenols (146). This may imply some sort of barrier due to the multiplicity change involved in such a reaction, that slows the reaction when it is at near-neutrality. This ion should also react with doubly stabilized carbon acids such as diketones, benzyl ketones, fluorenes, and some of the more stabilized anilines. The molecular oxygen anion usually functions as an electron transfer reagent, because of its low EA (0.44 eV). The chemical behavior of $O_2^{-\cdot}$ is distinct from that of $O^{-\cdot}$ (146). Aromatic compounds with good leaving groups (e.g., ArCl, ArNO$_2$) are converted to phenoxides by $O_2^{-\cdot}$ (147,148).

Acetate does not appear to have been utilized as a CI reagent ion, although it can be readily generated from acetic anhydride in methane. Because no acetic acid is nominally present in this mixture, self-clustering reactions are expected to be negligible. Acetate should deprotonate all carboxylic acids, almost all phenols, and only those alcohols with multiple electron accepting groups, such as $(CF_3)_2CHOH$. We predict that its bidentate structure should result in an increased affinity for adduct formation with proximate difunctional alcohols. Other substituted carboxylate ions can also be readily generated from their anhydrides, so that the reagent anions's basicity can be fine-tuned over a 26 kcal/mol range.

Chloride (115) is commonly used as an anion that is so weakly basic that adduct formation with available hydrogen bond donors is the predominant reaction (149). Certain structures are acidic enough to be deprotonated by chloride, however, such as the more acidic phenols, carboxylic acids, and 1,3-diones; this is seen experimentally, as a viable competitor to adduct formation (150,151). Chloride should also deprotonate some di- and trisubstituted carbon acids, such as malononitrile and fluoradene, with little or no adduct formation (8).

Is there any reagent anion that should yield essentially only adduct ions and

give little or no deprotonation or electron transfer? The conjugate bases of the strong acids may be good candidates for this: NO_3^-, PO_3^-, and $CF_3CO_2^-$ are all easily generated from precursors other than their conjugate acids (to minimize the concentration of good hydrogen bond donors, which could compete with the analyte), have high EAs and very low PAs. As oxyanions, they should inherently be good hydrogen bond acceptors, save for their low basicity. Perchlorate ion, ClO_4^-, is also a candidate, but no feasible source is yet known. Iodide and bromide are relatively poor at hydrogen bonding (151), so these halides are not as good a possibility. Attachment ions are observed experimentally, but only for acids which are in the lower half of the acidity scale (152). Reducing the source temperature also promotes adduct formation, for entropic reasons (115–117).

B. Electron attachment

Ion/molecule collision rates vary as the reciprocal of the square root of the reduced mass of the particles (153). For this reason, the collision rate of a free electron with a typical analyte can be 100 times or more faster than that for some reagent ion of typical mass 20–100. This has resulted in considerably greater sensitivity for electron attachment than for "normal" NCI (154).

Production of a stable, long-lived anion by electron attachment requires that the EA be positive (anion more stable than the neutral), that the rate of attachment be rapid, and that there be a mechanism for losing the excess energy so that rapid electron detachment does not occur. In CIMS, the latter is usually collisional stabilization; at 1 torr, there is an ion/molecule collision about every 30 ns. Examination of Figure 6, with some reasonable extrapolations of trends, indicates that aromatic rings with a single good electron-accepting group, such as a carbonyl, trifluoromethyl, cyano, or nitro, should have a bound radical anion. Two or more halogens on a benzene ring are required to have a bound radical anion. Naphthalene and larger polycyclic aromatic hydrocarbons also have positive EAs.

In practice, however, to observe $M^{-\bullet}$ in CIMS there appears to be a lower limit to the EA of ca. 0.5 eV. Polycyclic aromatic hydrocarbons (PAH) with EAs greater than 0.5 eV give $M^{-\bullet}$ ions as the most abundant ions in the spectrum, whereas PAHs with EAs less than 0.5 eV give little or no $M^{-\bullet}$ but a variety of fragment or impurity ions instead (155). The EAs used in the original analysis (155) were obtained from Hückel molecular orbital (MO) calculations. If experimental EAs for many of the PAHs (8) are used, however, there are cases in which molecules with EAs as high as 0.6 eV do not give $M^{-\bullet}$ (anthracene) and ones with EA as low as 0.4 eV (acenaphthylene) that do yield $M^{-\bullet}$ The cutoff is independent of temperature (155), so the cause does not appear to be an entropy-driven (113) electron-detachment reaction. Electron transfer from $M^{-\bullet}$ to trace O_2 (EA = 0.44 eV) is another possible reason, but $O_2^{-\bullet}$ and the products expected from its further reactions with the analytes (145–147) were not observed. Although a positive EA is obviously a necessary criterion for production of an observable radical anion, the rate of autodetachment of the excited radical anion relative to the collisional stabilization rate is also critical to successful production of electron attachment

ions. It may be that the electron attachment rate for compounds with EAs below 0.5 eV is too slow, because there are only a small number of states below this level in the manifold, and molecules in these states do not fragment competitively with the autodetachment process.

The observed EA threshold for electron attachment implies a practical limit for electron attachment to benzene rings: a nitro group, or more than one carbonyl, cyano, or trifluoromethyl group, or four or more halogens are required. These requirements are consistent with the common practice of derivatizing hydroxy groups with the pentafluorobenzoyl functionality (139,154,156). A second criterion for production of the parent radical anion is that there be no readily accessible dissociation channel. For example, $C_6F_5CH_2OPh$ should have a stable radical anion, but the most abundant ion is phenoxide (156).

Nonaromatic structures such as 1,2-diones and nitroalkanes form stable radical anions at the low EA end of this range, although the latter are prone to fragmentation to the uninformative ion NO_2^- (46,157). Halogenated species give abundant halide ions, but few ions at higher mass (122).

C. Positive chemical ionization

All organic compounds are capable of being protonated exothermically by CH_5^+; only CO_2, NO, CF_4, Xe, N_2, H_2, N_2, O_2, HF, and the smaller noble gases are weaker bases, in that order (8). Protonated methane, CH_5^+, can be generated by electron ionization of pure methane and subsequent ion/molecule reactions in the methane bath gas. Formation of the protonated forms of the weaker bases, however, requires electron ionization of mixtures of the neutral bases with hydrogen gas (69). All of these $(M + H)^+$ reagent ions are nonselective in that they protonate all organic structures. The drawback to this universality is that the considerable exothermicity for proton transfer to common organic functional groups results in appreciable energy deposition and leads to fragmentation of the product $(M + H)^+$ ions (158).

Isobutane acts effectively as the conjugate acid of the base 2-methyl-propene in CIMS. From Figure 1, it can be seen that $C_4H_9^+$ will not protonate water, alkanes, alkenes smaller than 2-methylpropene, nitriles, single-ring arenes, and the smaller esters, acids, aldehydes, and alcohols. The $C_4H_9^+$ will protonate all ethers save Me_2O and fluorosubstituted ones.

The NH_4^+ ion, generated, by electron ionization of ammonia and subsequent ion/molecule reactions, does not protonate ethyl ether, tetrahydrofuran (THF), halogenated hydrocarbons, simple alcohols, water, acetone, and ethyl acetate. This is useful since the commonly encountered solvents are transparent to NH_4^+; such solvents are often present as impurities in samples. Thus, ammonia CI has a special selectivity for nitrogen and phosphorous bases, relative to oxygen and carbon ones. For example, NH_4^+ should selectively protonate amides in the presence of other carbonyl compounds, although aryl ketones are sufficiently basic to give $(M + H)^+$ ions. The few non-nitrogen/phosphorous-containing groups that NH_4^+ will protonate include larger arenes capable of making benzyl ions,

multiply substituted anisoles, crown ethers, and other chelating difunctional compounds. Dimethoxyethane is just on the edge of exothermicity, but the mass law effect mentioned above for $(M + H)^+$ in M gas may shift the equilibrium against its formation. The use of ammonia as a CI reagent gas has been recently reviewed (7,158).

The alternative to formation of $(M + H)^+$ is adduct formation by the reagent ion or neutral:

$$(M + H)^+ + NH_3 \rightarrow MH^+ \cdot \cdot NH_3) \tag{22}$$

$$M + NH_4^+ \rightarrow M \cdot \cdot NH_4^+ \tag{23}$$
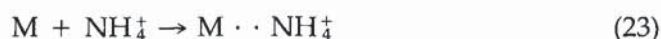
Adduct formation is not usually observed for nonpolar reagent gases such as methane and isobutane, because the adduct well depths are only about 3–10 kcal/mol. It is quite prominent, however, with NH_3 and other amines (7). The strength of such hydrogen or covalent bonds is a function of both the basicity of the analyte and the nature of the functional group (104–106). For amines, such proton-bound dimers are bound by 18–25 kcal/mol in enthalpy, and 10–17 kcal/mol in free energy (31,35). Adduct ions that are formed in ammonia CI are of fairly low abundance when the PA of the analyte is greater than that of ammonia (204 kcal/mol), because $(M + H)^+$ ions predominate then. Adduct ions are also observed only for analytes with PA $>$ 187 kcal/mol, or no more than 17 kcal/mol less basic than NH_3 (159). This threshold for adduct formation has been attributed to the strength of the bond being a function of the analyte's basicity: the bond becomes too weak to survive under the thermal conditions of the source if the PA is below that level (160). Typical $-NH^+ \cdot \cdot O-$ bonds fall in this range (31).

If one considers the reaction coordinate for NH_4^+ adduct formation with a base weaker than ammonia, however, a kinetic explanation for the cutoff presents itself, as shown in Figure 8. Case A represents analyte bases weaker than ammonia, but still stronger than the cutoff limit. When the ammonium ion encounters the base and forms an excited complex, the complex can exist in either the $NH_4^+ \cdot \cdot M$ well or the $H_3N \cdot \cdot {}^+HM$ well. If the analyte has a PA less than 187 kcal/mol, then Case B is the likely form of the potential, and the adduct ion is restricted to the $NH_4^+ \cdot \cdot M$ well. The number of degrees of freedom available to the complex is reduced with respect to Case A, and its lifetime is decreased with respect to dissociation back to M and NH_4^+. The excited complex is more likely to live long enough to have a stabilizing collision with the bath gas for Case A than for Case B.

Rudewicz and Munson (159) showed that if pure NH_3 is used as the reagent gas, the presence of $NH_4^+ \cdot \cdot NH_3$ ions results in considerable variation in the $MH^+/(M + NH_4)^+$ ratio with small changes in source conditions. These variations are greatly reduced if the reagent gas is dilute NH_3 in He or CH_4 (159).

Other reagent gases have been used for proton transfer CI. Diisopropyl ether (110) has essentially the same basicity as ammonia, but gives far less adduct formation, because of steric hindrance plus a reduced number of hydrogen bond donor sites (1 vs. 4).
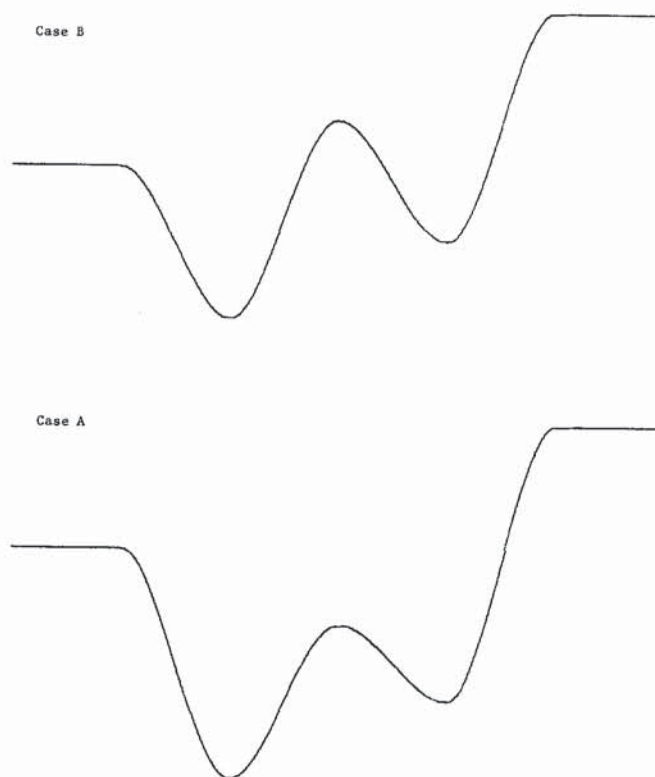
Figure 8. Energy-reaction coordinate diagram for varying endothermicities. For the reaction $A + BH^+ \rightarrow AH^+ + B$, the well on the left corresponds to $BH^+ \cdot \cdot A$, and the well on the right to $B \cdot \cdot {}^+HA$.

Reagent ions that act as Lewis bases are also known. Examples include Me_3Si^+ from $SiMe_4$ (161), CCl_3^+ from CCl_4 (162), CH_3^+ from Me_2O (163), and $ClCH_2^+$ from CH_2Cl_2 (164). Equilibrium affinity scales for these are not known, although for some ions they can be calculated from other data, as shown above in Section II.D. Also, the PA order for simple secondary amines, sulfides, and ethers is $N > S > O$ for similar alkyl substitution, but kinetically, alkylation with CH_3^+ prefers $S > N > 0$ (165).

A further caveat in interpretation involves Figure 8. If a proton can occupy two or more possible sites in a molecule, as in Case A, then fragmentation, and even the $(M + H)^+$ ion, need not be formed by reaction at the most basic site (166).

D. Self-protonation

"Self-CI," where a compound acts as its own CI reagent gas, is an important technique in FTMS (167,168) and can also be accomplished in conventional CIMS (169–171) and EIMS (172). In the simplest sense, the production of CH_5^+ in methane is a self-CI reaction. Although ionization of the gas can occur by a variety of reactions involving many fragment ions from a compound, a good general in-

Table IV.   Thermochemistry of the self-protonation reaction

BH	IP(BH)[a]	PA(BH)[a]	DH°(B-H)[b]	ΔH[c]
EtC≡N	273	193	90	−62
EtOH	244	190	93	−27
MeCF$_3$	297	150	107	−26
H$_2$O	291	166	119	−24
EtNO$_2$	251	185	100	−22
MeF	288	145	100	−19
NH$_3$	234	204	107	−17
Me$_2$C=O	224	197	93	−14
EtNH$_2$	202	217	93	−12
EtOEt	219	200	94	−11
Pyridine	213	220	110	−9
MeCl	259	163	101	−7
EtNMe$_2$	180	224	84	−6
H$_2$S	241	170	92	−5
MeCH=CH$_2$	224	179	86	−3
EtSH	214	190	87	−2
CH$_3$CH$_3$	277	140	101	−2
CH$_4$	288	132	105	−1
p-Nitroaniline	192	209	88	0
Me$_3$CH	244	163	96	3
EtPh	202	194	85	3
Ph$_2$C=O	214	210	110	4
EtSEt	194	205	92	6
MeBr	243	166	102	7
Aniline	178	211	92	17
C$_2$H$_4$	242	163	110	19
C$_2$H$_2$	263	154	125	22
Benzene	213	181	110	29
MeSSMe	171	196	94	41

[a]Ref. (8), kcal/mol

[b]Ref. (42), kcal/mol

[c]ΔH = DH°(B-H) + IP(H·) − PA(BH) − IP(BH), kcal/mol, for the reaction: BH$^{+\cdot}$ + BH → B· + BH$_2^-$

dication of whether self-CI will occur for a class of compounds is the thermo-chemical feasibility of the self-protonation reaction:

$$BH^{+\cdot} + BH \rightarrow BH_2^{\ddagger} + B\bullet \tag{24}$$

It can be shown that $\Delta H(24) = -IE(BH) + DH°(B - H) + IE(H\bullet) - PA(BH)$. Thus, high basicity, high ionization energy, and weak bond strength for a compound favor the self-protonation reaction. As the alkyl structure on a functional group is elaborated, the PA usually increases and the IE decreases, thus approximately offsetting any change and making ΔH (24) relatively constant for a series of homologues. These quantities are shown for compounds having a range of functional groups in Table IV.

Table IV reveals that most polar functional groups, as well as alkanes, are capable of self-protonation, but aromatics are a notable exception (173). The aromatic ring reduces the IE of the compound considerably, because the electron loss is from the aromatic π system rather than the attached functional group,

whereas the PA is not comparably affected. It is noteworthy that the reaction is close to thermoneutral for many of the species presented; for the archetypical case, methane, it is intriguing that all of the historic development of CIMS (174) rests on only 1 kcal/mol exothermicity.

The self-protonation reaction, however, is not a firm limit for self-CI. For example, if EI forms an ethyl cation from a structure, that ion can protonate any species more basic than ethylene, PA = 162.6 kcal/mol. This includes most organic functional groups, as well as larger alkanes.

For negative ions, although not all compounds produce such ions on electron ionization, self-CI can occur. A notable example is the class of halogenated compounds; these commonly yield a halide ion, which can then be solvated by its precursor neutral (175).

V. SUMMARY

Many properties of CIMS can be predicted and rationalized based on the thermochemistry developed from the equilibrium affinity scales that are now available. Although in the simplest sense, ionization of an analyte only requires that the affinity of the analyte be greater than that of the reagent ion for whatever process is occurring, ionization sensitivity and the branching ratio between two possible channels are often functions of the exothermicity of the processes involved. Knowledge of the thermochemistry can often reduce the effort of trial-and-error searching for optimum analytical conditions. Beyond CIMS, these scales have proved critical in exploring the mechanism of ionization in FAB (176,177) and in API mass spectrometry (143,145,148).

ACKNOWLEDGMENT

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