International Journal of Mass Spectrometry 200 (2000) 187–199

Thermochemical ladders: Scaling the ramparts of gaseous ion energetics

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Received 2 June 2000; accepted 14 August 2000

Abstract

The use of multiple overlapping gaseous ion–molecule equilibrium measurements to construct thermochemical ladders is reviewed. The types of relative thermochemical data, which may be obtained, are summarized and the types of measurements required to convert the relative equilibrium affinity scales to absolute thermochemical quantities are discussed. The important thermochemical scales produced include proton affinities, gas phase acidities, ionization energies, electron affinities, carbocation stabilities, hydrogen bond energies, Lewis acidities, and metal cation affinities. (Int J Mass Spectrom 200 (2000) 187–199) © 2000 Elsevier Science B.V.

Keywords: Gaseous ion energetics; Equilibria

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1. Historical background

During the early 1970s three techniques emerged for the study of gas phase ion–molecule reactions. High pressure mass spectrometry (HPMS) had been developed initially by Kebarle and Godbole as a means of probing the ionic processes believed to be important in radiation chemistry [1]. It soon became apparent, however, that the technique was ideally suited to the study of ion–neutral association equilibria,

$$A^+ + B \rightleftharpoons AB^+ \tag{1}$$

Using ion source pressures in the range of Torr to tens of Torr it was observed that steady state ratios of intensities of A^+ and AB^+ could be attained, which indicated that the reaction had reached equilibrium. From these intensities and the known pressure of B in the ion source an equilibrium constant could then be obtained,

$$K_{eq} = \frac{I_{AB^+}}{I_{A^+}}\frac{1}{P_B} \tag{2}$$

and from this the free energy change for the reaction, $\Delta G°$,

$$\Delta G° = -RT\ ln\ K_{eq} \tag{3}$$

When the ion source temperature was varied, the $\Delta H°$ and $\Delta S°$ for the association reaction could then be readily calculated, from a plot of ln K_{eq} versus T^{-1},

$$K_{eq} = \frac{-\Delta G°}{RT} = \frac{-\Delta H°}{RT} + \frac{\Delta S°}{R} \tag{4}$$

In this way, thermochemical data for association reactions could then be derived [2]. The flowing

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PII S1387-3806(00)00308-0

afterglow (FA) technique, developed by Ferguson and et al. [3], involves ion generation at one end of a flow tube with a fast flow of helium buffer gas and then adding reactant gases at various points downstream. From the known flow rate and reactant gas concentration, the reaction time could be determined as the arrival time for the reactant and product ions at the quadrupole mass spectrometer detector. This proved to be a very powerful method for the determination of rate constants for both bimolecular and termolecular ion–molecule reactions as shown, respectively, in the following equations:

$$A^+ + B \xrightarrow{k_5} C^+ + D \quad (5)$$

$$A^+ + B \xrightarrow{k_6[M]} AB^+ \quad (6)$$

The third technique, ion cyclotron resonance spectrometry (ICR), exploited the motion of charged particles in a perpendicular combination of strong magnetic and weak electric fields. In its original form the ICR experiment involved using the slow $\mathbf{E} \times \mathbf{B}$ drift of ions in this field combination to permit sufficient reaction time for ion–molecule reaction to occur at low pressures in the range from 10^{-7} to 10^{-5} Torr [4]. Using the ion cyclotron double resonance technique [5], ion–molecule reaction pathways could be unambiguously deduced and ICR experiments became a valuable means of probing ion–molecule reaction mechanisms. The ICR double resonance technique also permitted deduction of the exothermic direction of a given reaction, such as proton transfer, and this served as the basis for determination of qualitative orderings of proton affinities. Proton affinity (PA) is defined as the negative enthalpy change for the addition of a proton to a molecule, B, in the gas phase,

$$B + H^+ \rightarrow BH^+ \quad (7)$$

$$PA(B) = -\Delta H_7^0 = \Delta H_f^0(B) + \Delta H_f^0(H^+) - \Delta H_f^0(BH^+) \quad (8)$$

In 1970, McIver demonstrated that a reconfiguration of the electric field in the standard ICR cell permitted ions to be trapped for periods of time up to several seconds and, in this way, much greater ion–molecule interaction times were achievable at low pressure [6]. It was shown that this was also an excellent means of determining ion–molecule reaction rate constants. However, a clear breakthrough came about when Bowers et al. [7], showed that this trapped ion cell could be used to follow a reversible proton transfer reaction,

$$AH^+ + B \rightleftharpoons BH^+ + A \quad (9)$$

to equilibrium and, in so doing, to obtain equilibrium constants for proton transfer reactions. This marked the first demonstration of determination of accurate reaction thermochemistry from an exchange equilibrium. The importance and value of this method was quickly appreciated and immediately afterward both the HPMS [8] and FA [9] techniques were used similarly to obtain equilibrium constants for equilibrium exchange reactions. This has led, over the ensuing 30 years, to an explosion of thermochemical data that has tremendously benefited the interpretation of gas phase ion chemistry and the whole field of chemical dynamics in general.

2. Methodology

The use of thermochemical ladders to determine relative gaseous ion energetics is based on multiple, overlapping equilibrium constant determinations. Consider that an ion, either positive or negative, $Z^\pm$, is transferred between two compounds, A and B. The equilibrium exchange reaction is then given by

$$AZ^\pm + B \rightleftharpoons BZ^\pm + A \quad (10)$$

The equilibrium constant for Eq. (10) is obtained from the known ratio of pressures of A and B used in the experiment and the steady state intensities of the ions $AZ^\pm$ and $BZ^\pm$ once equilibrium has been reached. From the equilibrium constant the free energy change, $\Delta G°$, for the reaction may then be obtained from Eq.

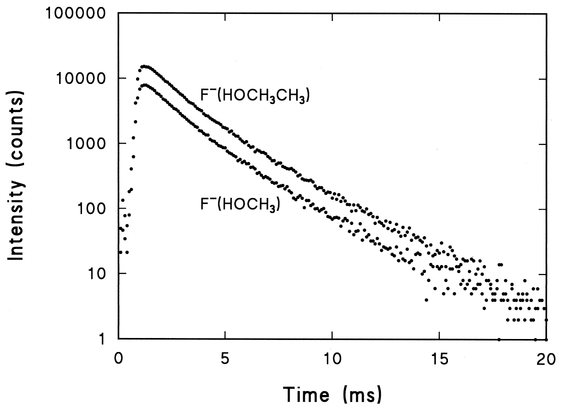


Fig. 1. Variation of ion intensities as a function of time after a 100 μs electron gun pulse in a high pressure ion source. The total ion source pressureis 4.8 Torr with partial pressures o 13.5 mTorr CH_3OH, 12.4 mTorr C_2H_5OH, and 1.9 mTorr NF_3. The remainder of the pressure is CH_4.

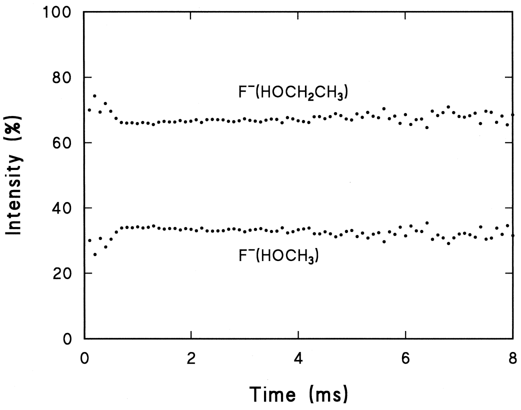


Fig. 2. Normalized ion intensities for the raw data described in Fig. 1.

(3). In practice, equilibrium constants on the order of 10^3 are the maximum which can normally be determined accurately. This dictates that free energy changes of approximately 4 kcal mol^{-1} at 298 K are the maximum links in any thermochemical ladder. Very occasionally, particularly in HPMS experiments, larger values of the equilibrium constant may be determined, but these are rare. For example, the data shown in Fig. 1 are the raw intensities of the F^- adducts of CH_3OH and C_2H_5OH followed as a function of time after ionization in a high pressure ion source. When these intensities are normalized, as shown in Fig. 2, it is apparent that a steady state ratio of ion concentrations is rapidly reached. The equilibrium constant for fluoride transfer can then be obtained from this steady state ion abundance ratio and the known ratio of pressures of methanol and ethanol in the ion source. If measurements are carried out only at a single temperature then only ΔG°, the standard Gibbs free energy change may be obtained. However, if the measurements are carried out over a series of temperatures, then both ΔH° and ΔS°, the standard enthalpy and entropy changes, respectively, may also be derived from a van't Hoff plot, Eq. (4). Such a plot is shown in Fig. 3 for the fluoride exchange equilibrium discussed previously. This equilibrium has been followed over a temperature range of greater than 100° which permits accurate ΔH° and ΔS° values to be derived. In this case ΔH° is determined to be -1.9 kcal mol^{-1} and ΔS° to be -2.3 cal mol^{-1} K^{-1}, for transfer of F^- from methanol to ethanol. When many equilibria involving a series of compounds are examined in such a way that each compound is linked simultaneously to species of lower affinity and higher affinity for the ion in question, then a thermochemical ladder is said to result. This can be illustrated in part by the ladder containing four compounds, A, B, C, and D shown in Scheme 1. Scheme 1

The lower case letters in the ladder mentioned previously can represent either ΔG°, ΔH°, or ΔS°. In the case illustrated here, the maximum number of measurements (six) interconnecting the four com-

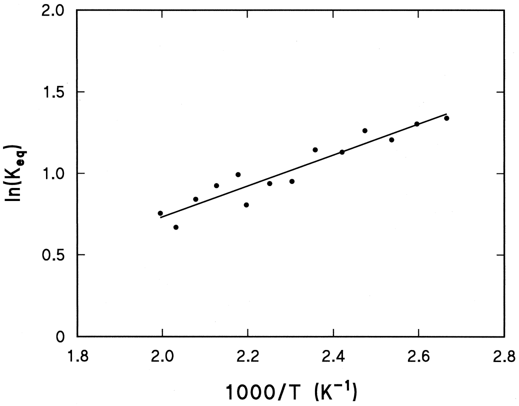
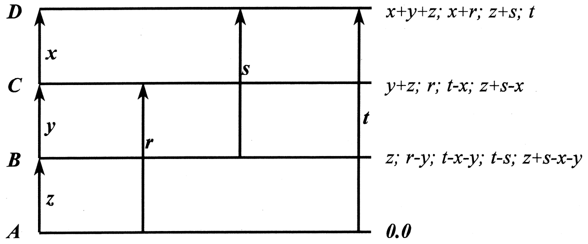


Fig. 3. van't Hoff plot for the F-exchange equilibrium between CH_3OH and C_2H_5OH.



Scheme 1.

pounds has been made. Using compound A as a reference point, the net change in the thermochemical quantity for each of the other compounds, relative to A, can then be given by at least four combinations of individually measured values, as shown to the right of the ladder. This represents the ideal situation but, in reality, for very long ladders many fewer measurements interconnecting all of the compounds will usually be made. Bartmess and Sorenson [10] have developed a computer program that determines the best possible "affinity" values of each compound from such ladders. In their analysis they point out the problems that can arise from so-called pendant values and fusion points. A pendant value is one for which the compound is tied to the ladder by a single experimental measurement. A fusion point is a compound that is connected to values both above and below itself in the ladder, but for which no other compound below is connected to a compound above. These two situations act to reduce the reliability of individual assignments as well as the overall relative scale values. Once an analysis of the overall scale has been accomplished a scale of relative thermochemical values for the relevant quantity is obtained. If the absolute values for the scale quantity are desired then one or more compounds must be assigned a value based on some other type of experiment that gives the absolute value of the thermochemical quantity. These data are often fairly difficult to obtain and may be subject to reassessment over time and this leads to further uncertainty in the scale developed. In the discussions below, of each of the different important scales which have been derived, the method used for assigning absolute values is outlined.

3. Proton affinities

Proton affinities were the earliest and by far the most extensively studied quantity using equilibrium thermochemical measurements. The first extensive proton affinity ladder to be published was that of Yamdagni and Kebarle [11] in 1976 using HPMS measurements of proton transfer equilibria at 600 K. This was followed in 1977 by an analogous ICR study of Wolf et al. [12], nominally at 300 K. This latter study was later shown to suffer from an uncertainty in the temperature at which the measurements were made due to heating of the ICR cell by the ionizing filament. In both cases the lower limit of the basicity scale investigated was H_2O and the upper limits extended up to very strongly basic amines. In 1980, using FA techniques, Bohme et al. produced a proton affinity ladder for very weak basic species with proton affinities less than that of CO [13]. Finally, using HPMS equilibrium measurements at 400 K, McMahon and Kebarle [14] linked the upper and lower regions of the proton affinity scale with a series of measurements involving bases as weak as CH_4 and as strong as H_2S. The equilibria examined in each of the above-mentioned studies allowed the construction of free energy ladders at the temperature of the experiment. These were converted to enthalpy ladders using statistical thermodynamic estimates of the entropy changes involved. In order to assign absolute values to the individual compounds a reference compound was then chosen. In the case of the first HPMS scale, isobutene was used as the anchor point for the scales based on a proton affinity value of 193 kcal mol^{-1}. This value had been assigned from the ionization energy of the *t*-butyl radical measured by Lossing and Semeluk [15], the C–H bond energy in *i*-butane assigned by Kerr [16] and the known heat of formation of *i*-butene [17]. The ICR scale was based on a proton affinity of NH_3[12] as 202.3 kcal mol^{-1} which had been apparently assigned in an unpublished study by the same authors. The FA scale had been anchored by the accurately known heat of formation of OH^+ and experiments in which oxygen atom had been generated in known concentrations to act as an equilibrium proton transfer equilibrium partner [13]. The

HPMS scale in the intermediate basicity regime was based on the proton affinity of C_2H_4 derived from PEPICO experiments which yielded an accurate heat of formation of $C_2H_5^+$ [18]. Since each of these scales was anchored to a different reference base there was a considerable extent of disagreement among the individual values assigned where there was overlap in the scales. In 1991 Meot-Ner and Sieck [19] carried out the first extensive series of temperature dependent proton transfer equilibrium measurements. This resulted in the first scale hat did not rely upon entropy estimates for proton transfer and gave a completely experimental ladder of enthalpy changes. These authors anchored their scale at *i*-butene with an assigned proton affinity of 196 kcal mol^{-1} derived from a newer *t*-$C_4H_9^+$ heat of formation based on appearance energy measurements of McLoughlin and Traeger [20]. The data obtained showed a much larger difference between the proton affinities of *i*-butene and NH_3 which resulted in a proton affinity value of NH_3 of nearly 208 kcal mol^{-1}, much higher than had been previously considered to be viable. This high value for the proton affinity of ammonia and the implied difference of greater than 40 kcal mol^{-1} between the proton affinities of H_2O and NH_3 raised serious concerns about the validity of much of the existing proton affinity scale above H_2O. As a result, Szulejko and McMahon [21] undertook a systematic temperature dependent investigation of the proton affinity region between *i*-butene and NH_3 and confirmed the difference found by Meot-Ner and Sieck. In addition, at this time, Smith and Radom [22] carried out a series of high level ab initio calculations at the G2 level of theory to determine proton affinities of many key compounds in the proton affinity scale. Their results suggested that the accepted proton affinity of *i*-butene was in fact in error. In order to settle the large number of uncertainties arising from this data, Szulejko and McMahon [23] then undertook an examination of temperature dependent proton transfer equilibria over nearly the entire possible range of the proton affinity scale. This scale spanned a range of proton affinities of over 100 kcal mol^{-1}, from N_2 to *t*-butyl amine and included some 50 compounds. As an anchor for the entire scale, the proton affinity of CO was chosen since the heat of formation of HCO^+ appeared to be the most accurately and firmly established cation heat of formation permitting the calculation of a proton affinity of a stable neutral molecule [24]. Using this scale, excellent agreement was obtained for the proton affinities of other compounds, such as N_2, CO_2, C_2H_4, H_2O, H_2S, C_3H_6, $(CH_3)_2CO$, and NH_3, which could be obtained from appearance energy measurements. The glaring exception to this excellent agreement was for *i*-butene where a value 4.3 kcal mol^{-1} lower than that accepted at the time was found. This new value of 191.7 kcal mol^{-1} for the proton affinity of *i*-butene was in excellent agreement with that calculated by Smith and Radom. At the same time, Baer and co-workers [25] had carried out new PEPICO measurements of the appearance energy of *t*-$C_4H_9^+$, which resulted in a proton affinity for *i*-butene in excellent agreement with the new equilibrium and ab initio values. The latest NIST compilation of proton affinities [26] has relied heavily on the experimental equilibrium ladders of Szulejko and McMahon [23] and Meot-Ner and Sieck [19]. These two scales contain a sufficient number of compounds that a convenient reference for almost any new proton affinity measurement is readily available. The authors of the NIST compilation [26] have however used ab initio calculated entropies in general, in preference to experimental values, in the assignment of absolute proton affinities. As of this writing, in this author's opinion, there still exist a significant number of anomalies in the NIST compilation.

4. Gas phase acidities

The gas phase acidity of a molecule AH is defined as the Gibbs free energy change for the deprotonation of AH,

$$AH \rightarrow A^- + H^+ \tag{11}$$

at 298 K. The enthalpy change for this reaction is simply the proton affinity of the anion, A^-, and, as such, anion proton affinities comprise a data set entirely analogous to the proton affinities of neutral molecules. This heterolytic bond dissociation process can also be understood in terms of a homolytic bond dissociation followed by ionization of the hydrogen atom and electron attachment to A. In this respect the anion proton affinity can then be decomposed into the enthalpy changes associated with these processes,

$$\mathrm{PA(A^-)} = D(\mathrm{A{-}H}) - \mathrm{EA}(A) + \mathrm{IE}(H) \tag{12}$$

where D(A–H) is the AH homolytic bond dissociation enthalpy, EA(A) is the electron affinity of A and IP(H) is the hydrogen atom ionization energy, all at 298 K. For the diatomic hydrogen halides the electron affinities and bond dissociation energies are well established from spectroscopic measurements and as such these compounds provide excellent accurate anchors for any scale of equilibrium proton transfer measurements between anions,

$$\mathrm{X^-} + \mathrm{YH} \rightleftharpoons \mathrm{Y^-} + XH \tag{13}$$

The first series of equilibrium gas phase acidities to be published was that of Yamdagni and Kebarle in 1973, which linked six carboxylic acids to HCl by using HPMS equilibrium measurements [27]. Later that same year McIver and Silvers [28] reported gas phase acidity measurements from ICR experiments for a series of 15 phenols. No attempt to anchor that scale to a reference standard was made. In the case of both studies, only single temperature measurements were done and no attempt was made to evaluate entropy changes associated with proton transfer. McMahon and Kebarle [29] later published a gas phase acidity scale containing 50 benzoic acids and phenols from which a detailed understanding of intrinsic substituent effects on aromatic systems could be obtained. This scale was also linked to HCl as a primary reference, however once again no temperature dependence was studied and entropy changes were assumed to be negligible. A similar study, involving carbon and nitrogen based acids, including approximately 30 compounds was also carried out by the same authors [30]. This carbon acid acidity scale was later expanded upon by Cumming and Kebarle [31] who also used approximate statistical thermodynamic arguments to estimate entropy changes associated with the individual proton transfer reactions involved. The first attempt to establish a scale of gas phase acidities incorporating species more weakly acidic than HF was carried out by Bartmess et al. [32]. Their ICR study also made entropy estimates to relate the equilibrium data to HF as a primary standard for anion proton affinities. In the intervening period there have been many additions of compounds and groups of compounds to the gas phase acidity literature. Bartmess has reviewed the state of the gas phase acidity scale in 1989 [33] and 1996 [34] and the NIST database [35] contains over 1000 entries, many of them arising from equilibrium measurements. It is important to note, however, that there has been no systematic experimental study of the temperature dependence of gas phase acidities and, for this reason, the proton affinities of anions must be regarded as being less firmly established than the analogous proton affinity data for neutral molecules.

5. Ionization Energies

Charge transfer equilibrium between pairs of compounds,

$$\mathrm{A^+} + \mathrm{B} \rightleftharpoons \mathrm{B^+} + \mathrm{A} \tag{14}$$

was first investigated using ICR techniques by Anicich and Bowers [36] and using HPMS techniques by Meot-Ner and Field [37]. This type of equilibrium study requires that there be no other reaction of the parent radical cations occurring which could compete with charge exchange. For most organic molecules this is unlikely and thus limits the general utility of the method. Meot-Ner and Field [37] obtained relative free energies of ionization for a series of substituted benzenes and anchored their scale of ionization energies using the accurately established ionization energy of benzene. Lias and Ausloos [38] later showed that excellent agreement with spectroscopically determined ionization energy values could be obtained for the relative ionization energies of NO, benzene, and furan if corrections of the spectroscopic data to 298 K were made. The authors carried out some limited temperature dependent equilibrium measurements to demonstrate the relationship between adiabatic ionization energies and the enthalpies of ionization determined by equilibrium means and they reported data for a large number of substituted benzenes. Meot-Ner [39] later demonstrated that relative free energies of ionization for a series of polycyclic aromatic hydrocarbons at 550 K were readily obtainable. He also made the assumption that these relative values were equal to the relative enthalpies of ionization as well as to the difference in adiabatic ionization energies. Sieck and Mutner [40] subsequently carried out a temperature dependent equilibrium study of the relative ionization energies of a series of cycloalkanes. Another, particularly striking example of the use of thermochemical ladders to determine adiabatic ionization energies was that by Meot-Ner et al. [41] involving hydrazines where ionization energies could not be determined readily by traditional methods because of the large geometry changes between the ion and the parent neutral molecule. The fact that there are significantly fewer investigations of equilibrium charge transfer, compared to proton transfer, is a reflection of the fact that ionization energy data are much more readily available through very accurate photoionization measurements.

6. Electron affinities

Unlike ionization energies, there are very few electron affinities of stable neutral molecules which have been accurately determined by means other than equilibrium measurements. Many electron affinities of radical species have been determined by techniques such as negative ion photoelectron spectroscopy [42] but these are not useful reference species for equilibrium experiments since the neutral radical species cannot be introduced into the experiment at known partial pressures. The first negative ion electron transfer equilibrium

$$A^- + B \rightleftharpoons B^- + A \tag{15}$$

experiments were carried out by McIver and coworkers [43] who used ICR experiments to demonstrate that the relative free energies of electron attachment to quinones could be obtained. Later, Fukuda and McIver [44] extended this method to a series of nitrobenzenes and SO_2. At the time, the electron affinity of SO_2 was not regarded as having been well established and no compound of well-known electron affinity was included in the series of measurements carried out. As a result, the free energies of electron transfer obtained in the ICR experiments were not used to obtain absolute electron affinities of the compounds studied. Subsequently, Kebarle and coworkers, in a series of articles [45], presented an extensive body of equilibrium electron transfer data for well over 100 compounds including substituted benzenes, quinones, anhydrides, as well as organometallic species. The scale was anchored to the electron affinity of SO_2 which was by then taken to have been accurately determined [46]. For the most part, temperature dependent equilibrium measurements were not carried out and the free energies of electron attachment were converted to enthalpies of electron attachment using statistical thermodynamic arguments. The body of data obtained from these experiments however remains the largest single collection of electron affinities available from any single experimental method.

7. Carbocation stabilities

Equilibrium measurements in which either a hydride or a halide ion is transferred between pairs of carbocations,

$$R_1^+ + R_2X \rightleftharpoons R_2^+ + R_1X \tag{16}$$

provide a measure of the relative carbocation stabilities. Solomon and Field [47] first demonstrated that HPMS techniques could be used to examine hydride transfer equilibria to obtain accurate relative hydride affinities of the *t*-butyl and *t*-pentyl cations. They later examined hydride exchange equilibria for a limited series of C_4 to C_7 hydrocarbons and established several new carbocation enthalpies of formation [48]. Kebarle and co-workers [49] have also examined hydride transfer equilibria by using HPMS experiments to obtain insight into the relative stabilities of interesting carbocations such as benzyl, tropyl, and norbornyl. The use of fluoride transfer equilibrium to demonstrate the relative stabilities of the CH_2F^+ and CHF_2^+ cations was first shown by McMahon et al. [50] and isolated subsequent examples of the use of fluoride, chloride, and bromide transfer equilibria to establish relative cation stability orders exist [51]. No extensive ladder of affinities of this type exists, however, largely due to the wide range of values for these quantities which renders numerous overlapping equilibrium measurements very difficult. In addition, very accurate heats of formation of key carbocations to use as reference points are not numerous.

8. Hydrogen bond strengths

8.1. Proton bound dimers

Although HPMS investigations had been demonstrated to be capable of determining bond strengths in proton bound dimers,

$$BH^+ + B \rightleftharpoons BHB^+ \tag{17}$$

by using clustering equilibrium measurements, no systematic investigation of these species had been undertaken. Normally, adduct ions such as proton bound dimers are not readily obtainable, at the low pressures of ICR experiments, since the third body collisional stabilization process is too slow to permit their formation. However, Clair and McMahon [52] demonstrated that, from two independent sequences of bimolecular reactions in mixtures of H_2O and $(CHF_2)_2O$

$$CHF_2^+ + (CHF_2)_2O \rightarrow CHF_2OCHF^+ + CHF_3 \tag{18}$$

$$CHF_2OCHF^+ + H_2O \rightarrow CHF_2OH_2^+ + HCOF \tag{19}$$

$$CHF_2OH_2^+ + H_2O \rightarrow (H_2O)_2H^+ + CF_2 \tag{20}$$

and

$$H_3O^+ + (CHF_2)_2O \rightarrow (H_2O)(HCOF)H^+ + CHF_3 \tag{21}$$

$$(H_2O)(HCOF)H^+ + H_2O \rightarrow (H_2O)_2H^+ + HCOF \tag{22}$$

the proton bound dimer of H_2O could be readily generated. Then, if a base, B, of proton affinity greater than water, is added to the ICR cell H_2O can be replaced from the proton bound dimer in a sequence of ligand switching reactions,

$$(H_2O)_2H^+ + B \rightarrow BH(OH_2)^+ + H_2O \tag{23}$$

$$BH(OH_2)^+ + B \rightarrow BHB^+ + H_2O \tag{24}$$

Finally, if two bases, B_1 and B_2, are simultaneously present, the two ligand switching equilibria may be observed,

$$BHB^+ + A \rightleftharpoons BHA^+ + B \tag{25}$$

$$BHA^+ + A \rightleftharpoons AHA^+ + B \tag{26}$$

From the equilibrium constants obtained, the relative free energies of the hydrogen bonds can be determined [53]. The scale of strong hydrogen bond energies obtained was anchored to the value for the proton bound dimer of dimethyl ether for which Kebarle and co-workers had obtained accurate energetics from HPMS clustering measurements [54]. The ICR ligand switching equilibrium experiments did rely on entropy estimates and, as a result, the conversion from free energies of hydrogen bonding to enthalpy values could have resulted in some additional uncertainty. One important conclusion drawn from these experiments was that nearly all oxygen *n*-donor bases, regardless of functional group type, have symmetric proton bound dimers with a bond strength of 30.7 ± 1 kcal mol^{-1}. Further, the bond strengths in unsymmetrical proton bound dimers were shown to be roughly equal to the value in the symmetrical proton bound dimer ± one-half of the difference between the proton affinities of A and B. This relationship has proven to be very useful in the estimation of strong hydrogen bond strengths in many species for which equilibrium experiments cannot be done, such as those involving distonic ions.

8.2. Anionic hydrogen bonded adducts

A similar group of ICR studies has been carried out for anionic hydrogen bonded systems as well. Hydrogen bonded adducts of F^- and alkoxide ions may be generated in ICR experiments using the reaction of Riveros et al. [55] between these anions and formate esters,

$$X^- + HCO_2R \rightarrow X^- \cdots HOR + CO \tag{27}$$

Larson and McMahon [56], using F^- as the reagent anion, then showed that fluoride exchange equilibria,

$$F^- \cdots HA + BH \rightleftharpoons F^- \ldots HB + A \tag{28}$$

could be examined in mixtures of various protic species to obtain accurate relative energetics of hydrogen bonds to fluoride ion. Once again, only single temperature equilibria were studied and statistical thermodynamic estimates were made in order to obtain enthalpy changes from the experimentally determined free energy changes. The resulting fluoride binding energy scale was anchored to the HPMS clustering measurements of Kebarle and co-workers for $F^-(H_2O)$ [57]. Subsequently, HPMS clustering measurements of F^- onto alcohols by Bogdanov et al. [58] have shown that the data derived from the ICR switching equilibria for alcohols are valid. This study also included the hydrogen bond energy in the bifluoride ion, FHF^-, which was assigned as 38.6 kcal mol^{-1}. This is an important quantity because this is thought to be the strongest possible hydrogen bonded species. Wenthold and Squires [59] later carried out threshold collision-induced dissociation experiments and G2 ab initio calculations on FHF^- and concluded that the fluoride binding energy in this species should be some 7 kcal mol^{-1} higher than that deduced from the fluoride exchange equilibrium ladder. It is not clear whether this might be an isolated discrepancy in the thermochemical ladder, due to difficulties in handling HF, or if there should be a general shift in the scale of fluoride ion affinities in this region of the scale. Subsequent HPMS clustering measurements for F^- onto *t*-butyl alcohol [58] confirmed however that this lower region of the scale, in the vicinity of 33 kcal mol^{-1}, was accurate as originally determined by Larson and McMahon. Bartmess and co-workers [60], using an analogous reaction of alkoxide anions with formate esters to generate alkoxide–alcohol adducts, examined solvent switching equilibria in an ICR spectrometer to obtain a scale of hydrogen bond energies for a series of anion–alcohol clusters. Their scale had been anchored to a preliminary HPMS value by Caldwell and Kebarle for $(CH_3O)_2H^-$ of 21.8 kcal mol^{-1}. In later HPMS experiments [61] this value was shown to actually be 29.3 kcal mol^{-1} and therefore the absolute values of the hydrogen bond energies reported by Bartmess and co-workers should be revised upwards by this difference. Larson and McMahon also demonstrated that the $ClCO_2{}^-$ ion generated by the reaction of Cl^- with methyl chloroformate,

$$Cl^- + ClCO_2CH_3 \rightarrow ClCO_2^- + CH_3Cl \tag{29}$$

is an efficient chloride transfer reagent to many molecules,

$$ClCO_2^- + AH \rightarrow Cl^- \ldots HA + CO_2 \tag{30}$$

In this way chloride transfer equilibria could then also be examined readily [62]. The scale of chloride ion affinities obtained was anchored to the value for *t*-C_4H_9OH which had been determined from HPMS clustering measurements by Kebarle and co-worker [63]. More recent measurements of this clustering equilibrium indicate that this value is probably about 1 kcal mol^{-1} higher than originally reported, in which case the chloride affinity scale of Larson and McMahon should be raised uniformly by this value. Larson and McMahon [64] also performed similar ICR experiments on cyanide adducts of Bronsted acids using reactions of either CN^- or Cl^- with cyanoformate esters to generate $NCCO_2^-$ which subsequently acted as a CN^- donor. The cyanide affinity scale which resulted was anchored to the enthalpy of binding of CN^- to H_2O of 13.8 kcalmol^{-1} which had been determined by Payzant et al. [65]. Larson et al. [66] later made a series of HPMS clustering equilibrium measurements with the net result that the ICR Bronsted acid CN^- affinity scale should be adjusted downward by approximately 1 kcal mol^{-1}.

9. Lewis acidities

Larson and McMahon [67] used the same techniques as those described above for hydrogen bonded adducts, to generate Lewis acid adducts of fluoride, chloride, and cyanide ions. The equlibria of these species were interleaved with the scales of fluoride, chloride, and cyanide ion affinities of hydrogen bonding molecules and, as such, the corrections to the scales described previously should also be applied to the originally published Lewis acidity scales.

10. Metal cation affinities

In 1975 Beauchamp and co-workers [68] reported that Li^+, generated by thermionic emission from a filament coated with lithium salts, would react with alkyl chlorides via an elimination reaction which yielded an olefin bound to Li^+,

$$Li^+ + i{-}C_3H_7Cl \rightarrow Li(C_3H_6)^+ + HCl \qquad (31)$$

Allison and Ridge [69] later showed that the same type of reaction was possible with alcohols to also yield Li^+ bound to H_2O with elimination of the olefin,

$$\begin{aligned} Li^+ + t - C_4H_9OH &\rightarrow Li(C_4H_8)^+ + H_2O \\ &\rightarrow Li(H_2O)^+ + C_4H_8 \qquad (32) \end{aligned}$$

In 1979, Freiser and co-workers [70] showed that a host of atomic metal cations could be generated by direct laser ablation of a metal surface contained within an ICR cell and their subsequent bimolecular reactions studied. Staley and co-worker [71] then adopted this methodology and the reaction types developed by Beauchamp and co-workers [68] and Ridge and co-worker [69] to generate small molecule complexes of many different metal ions. Frequently a second elimination with the alkyl halide or alcohol is observed such that two ligand complexes of olefin and/or HX are generated ($HX = H_2O$, HCl) [72]. From the study of the subsequent two ligand switching equilibria in the ICR cell equilibrium constants were derived and relative free energies of ligand binding obtained for a wide variety of two ligand complexes of Cu^+ [73], Co^+ [74], Ni^+ [75], and $FeBr^+$ [76] were obtained. In addition single ligand switching equilibria for monoligated complexes of Al^+ [77] and Mn^+ [78] were examined. These measurements yielded only relative free energies of binding and, at the time no real attempt was made to estimate the entropy changes associated with the ligand switching reactions. In addition, no data were available to give an absolute value of ligand binding energies to the complexes so that the scales remained only relative ones. However, more recently, single and double ligand binding energies for several of the key adducts in Staley's scales have become available, either from threshold CID measurements [79] or from laser ablation HPMS clustering measurements [80]. Thus the potential exists, with some attempt to make entropy considerations, to put Staley's relative ligand binding data on an absolute enthalpy footing. For the past 20 years Taft and co-workers have used the abovementioned reaction sequence to generate Li^+ adducts to examine ICR ligand exchange equilibria of many compounds to Li^+ [81]. The original, extensive scale of Li^+ affinities was anchored to a Li^+–CH_2O binding enthalpy which was attributed to Beauchamp and co-worker [82]. More recently, Rogers and Armentrout [83] have pointed out that this absolute value is in error and a new, expanded scale of Li^+ affinities has very recently been published. This new scale is anchored to Li^+ binding enthalpies of Rogers and Armentrout for H_2O, CH_3OH, and $(CH_3)_2O$ which have been related to the experimentally measured relative free energies by using ab initio calculated entropies of all reaction participants. In a very recent study, McMahon and Ohanessian [84] have used Fourier transform ion cyclotron resonance (FTICR) exchange equilibria involving single ligand complexes of Na^+. In this case Na^+ was generated directly from electron impact ionization of sodium vapor in the external source of an FTICR spectrometer system. The Na^+ ions thus generated reacted with t-C_4H_9Cl in a manner analogous to Eq. (31) for formation of Li^+ adducts. The resulting $Na^+(C_4H_8)$ adduct then reacts with a mixture of species A and B, present in excess, such that Na^+ transfer equilibrium can be established,

$$Na^+(A) + B \rightleftharpoons Na^+(B) + A \qquad (33)$$

The relative Na^+ affinity scale included over 50 compounds and was anchored by HPMS clustering equilibrium measurements of Na^+ onto NH_3, CH_3NH_2, and CH_3OH [85]. In addition, very high level ab initio calculations were carried out on each of the ionic and neutral participants in nearly every FTICR equilibria examined such that accurate assessments of the entropy changes involved could be made to convert the measured free energy changes to enthalpy changes. An extremely impressive extent of agreement was obtained between absolute sodium ion affinities thus obtained and those calculated directly via ab initio methods. In addition, for many of the compounds examined, threshold CID measurements of Armentrout and Rodgers [86] were also available and the agreement with these values was also very impressive.

11. Summary

In the previous discussion, an attempt has been made to summarize each of the important reaction types for which extensive series of equilibrium measurements have been made in a single laboratory to construct a thermochemical ladder. In contrast, no attempt has been made to include the myriad of equilibrium data that have been obtained in investigations, which had a goal other than to construct a thermochemical ladder. In so doing, it is readily acknowledged that many important thermochemical measurements have been omitted from this discussion. However these latter data are included in the NIST compilation [87] of thermochemical data for gaseous ions and the individuals responsible for that work have carried out the difficult task of inserting these isolated thermochemical values into the larger context of a master thermochemical scale. Even when viewed alone, without the considerable data from these other experiments, the thermochemical ladders presented here must be acknowledged as having had an enormous impact on gas phase ion chemistry and on chemical energetics and dynamics in general. The extensive series of values produced have permitted a detailed analysis and interpretation of substituent effects which has greatly expanded our chemical intuition for the understanding of gaseous ionic behavior. In addition, the database developed has provided an energetic basis for the understanding of the dynamics of a wide variety of ion–molecule reactions. At this juncture, it may be generally considered that the database for gaseous ion energetics is more extensive and more accurate than that which exists for stable neutral molecules and this accomplishment is due, in no small measure, to the substantial contributions made from thermochemical ladders. It is now also apparent that the use of high level ab initio calculations to supplement the experimental equilibrium measurements is an invaluable aid to the reliability and accuracy of the thermochemical values deduced.

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