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Correlating thermochemical data for gas-phase ion chemistry

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Abstract

This article presents a brief review of correlation schemes which relate ionization energies, ionic heats of formation, proton affinities and heterolytic bond strengths with some simple property of the ion, most commonly its size. The schemes reviewed here have mainly been developed for homologous series and simple atom or group substitutions at charge-bearing sites. The utility of such schemes is illustrated by appropriate examples. (Int J Mass Spectrom 200 (2000) 277–284) © 2000 Elsevier Science B.V.

1. Introduction

Knowledge of the energetics of gas-phase ion dissociations is a significant step towards an understanding of the physicochemical processes involved. Indeed, without a well-developed potential energy diagram showing the relative energy levels for the ion(s) under study and their products of dissociation and/or rearrangement, an investigation cannot be considered complete.

Empirical methods for estimating the thermochemical properties, standard enthalpy and entropy of formation, $\Delta_f H^0$ and $\Delta_f S^0$, and constant pressure heat capacity, C_p , for neutral molecules and free radicals have long been associated with the work of Benson [1]. Benson's schemes, with which it is assumed the reader is familiar, are all based on the principle of additivity and are especially applicable therefore to homologous series of molecules. Correction terms for structural complications are well known for ring-strain, stereoisomeric effects, and so on. The thermo-

chemical reference data on which these schemes are based are all experimental and comprise a rather small archive; the collection of Pedley, Naylor and Kirby [2] contains thorough, carefully evaluated data for some 3000 $\Delta_f H^0$ values for organic compounds. The same and estimated values can be found in print [3] and at the NIST web site [4], the chief databases for thermochemistry of ions and neutrals. New experimental data for unexceptional molecules or radicals should be close to the value predicted from additivity considerations.

In the case where there is no experimentally determined $\Delta_f H^0$ and the necessary Benson terms are missing, only three solutions suggest themselves. One is to perform the necessary experiment (e.g., measure a heat of combustion), a second is to calculate the $\Delta_f H^0$ using a sufficiently high level of theory and the third is to use chemical intuition or argument by analogy.

For cations, simple additivity does not work, because the ionization energies (IE) of molecules and free radicals, even in homologous series, are not directly proportional to, for example, the number of CH_2 groups therein. Thus the equation:

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$$\Delta_f H^0 [\text{ion}] = \text{IE}[\text{molecule}] + \Delta_f H^0[\text{molecule}]$$

can not be transformed into a simple additive function.

The purpose of this short article is to show that simple correlation schemes exist that can reproduce or predict many ionic heats of formation to within a few kcal mol^{-1} ($\pm 8 \text{ kJ mol}^{-1}$) and that, in their use, require some insight into the physicochemical nature of the ion to be evaluated. Most important is the formal charge site within the ion. Appropriate examples of the use of the various relationships will be given.

2. Ionization energies

By definition, the IE of a molecule corresponds to the energy required to remove an electron therefrom. However two IEs are often quoted for each molecular species, the adiabatic, IE_a , and the vertical, IE_v values. The latter refers to the energy difference between the ground state of the neutral and the level at which vertical (Franck–Condon) excitation cuts the potential surface of the ground ionized state (see Fig. 1). Photoionization (PI) is a vertical process and so IE values determined thereby provide IE_v data. An adiabatic IE corresponds to the ground-state to ground-state energy difference between the ion and the neutral (Fig. 1). In cases where there is little or no geometry change in going from the neutral to the ion, then IE_a and IE_v are the same. The measurement of IE_a for species that involve a significant geometry difference is not easy, because identifying the ionization threshold is not straightforward. A careful electron impact ionization energy measurement, in contrast with photoionization, solely a vertical process, should allow the determination of IE_a even in cases where the threshold cross-section is fairly small, because the former ionization process does not proceed strictly vertically. In cases where the geometry change is significant, and therefore the cross-section for adiabatic ionization is negligible, the IE obtained should only be considered as an upper limit to the IE_a [5].

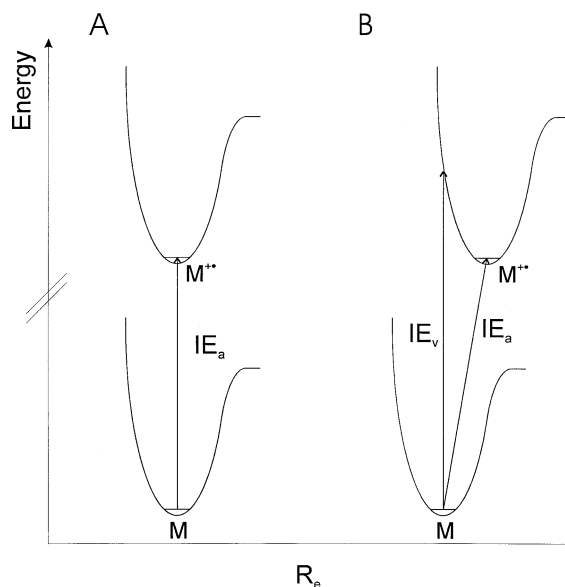


Fig. 1. Adiabatic and vertical ionization energies (IE_a and IE_v , respectively) for (A) a system where the geometries of the ground-state neutral (M) and ground-state ion (M^+) are the same and (B) a system where the geometries of the ground-state neutral (M) and ground-state ion (M^+) are different.

Photoelectron spectroscopy [6,7] is also an important method for obtaining IE_v values, but the same caveats apply to the estimation of IE_a therefrom.

Examples of classes of compound for which the cross-sections for adiabatic ionization are small are alkanes, cycloalkanes and cyclic ethers. Photoionization of $n\text{-C}_5\text{H}_{12}$ gave an IE value of 10.35 eV, whereas an energy-selected electron impact measurement gave an IE value of 10.22 eV [8]. This value is consistent with the correlation of IE_a with molecular size (see the discussion below).

The number of reliable experimental IE values is distressingly small and so any empirical relationship that accurately correlates the existing data cannot fail to find use.

Bachiri et al. [9] were the first to propose an equation for estimating IE values. Their empirical scheme relied on the following complex equation:

$$\text{Log}_{10} \frac{\text{IP}[\text{R}_1\text{XR}_2] - \text{IP}_\infty}{\text{IP}_0 - \text{IP}_\infty} = 0.106[\text{I}(\text{R}_1) + \text{I}(\text{R}_2)]$$

where X is a functional group (e.g., alkene, alkyne, aldehyde, ketone, ether, mercaptan or thioether) and R_1 and R_2 are alkyl groups. IP_0 is the ionization energy of the reference compound, where $R_1 = R_2 = H$, I is a constant, characteristic of each alkyl group and IP_∞ is a constant for each type of compound (corresponding to an extrapolated IP to infinite ion size). Although reliable IE values can be obtained from this scheme, the equation does not lend itself to a simple graphical presentation, to show for example, substitution effects, and therefore does not provide any straightforward physicochemical rationale for the values obtained.

Holmes et al. [10] proposed a second and simpler approach, which involved determining the effect of size (expressed by the number of atoms, n) on the ionization energy. Along a homologous series of compounds (sequential addition of a methylene group), the IE_a falls at a decreasing rate with increase in size. Plotting the IE_a against the reciprocal of ion size, $1/n$ produces a straight line. Combining the additivity of neutral thermochemistry with this reciprocal relationship, produced a general equation:

$$\Delta_f H^0[\text{ion}]^{++} = A - Bn + C/n$$

where A , B and C are constants for homologous alkanes, olefins, alkynes, alkanols, aliphatic ethers, aliphatic aldehydes and ketones, alkanolic acids, alkyl chlorides, bromides and iodides. Correction terms were included for chain branching, double-bond position and asymmetry effects.

The slope of the line in an IE vs $1/n$ plot is indicative of the ability of the ionized functional group to retain the charge. For example, the slope of the line for the alkanes, C_2 to C_{11} , is steeper than that for the series of homologues starting with CH_3NH_2 , CH_3OH or CH_3Br (Fig. 2). Thus, in alkanes, the charge is delocalized throughout the ion, in contrast with the other species shown where the charge is localized at the heteroatom.

Some pertinent comments on charge delocalization can be made for di- n -alkyl ethers and cyclic ethers on the basis of such plots [8] (Fig. 2). The IE_a versus $1/n$ lines for the homologous ROR and cyclic ethers are

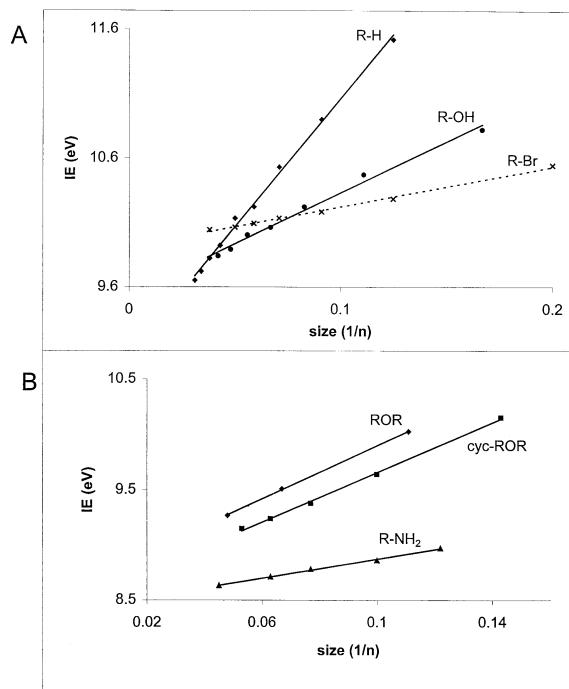


Fig. 2. Effect of size ($1/n$, where n is the number of atoms) on the ionization energy (IE) of (A) \blacklozenge alkanes; \bullet alkanols; \times alkyl bromides and (B) \blacklozenge dialkylethers; \blacksquare cyclic ethers; \blacktriangle n -alkylamines.

parallel indicating that the stabilizing effect is the same irrespective of whether the methylene group is added to a straight chain or a cyclic species. Furthermore, that a straight line relationship is observed for the cyclic ethers also indicates that the ring strain in the smaller homologues does not contribute any effect to the IE_a .

Therefore, plots of IE_a versus the reciprocal of ion size for a series of homologues provides information on the extent of charge delocalization as well as leading to IE_a values for missing members of a series and the possible correction of erroneous data.

3. Proton affinities

Proton affinity (PA) is another molecular property that varies with ion size in a similar manner:



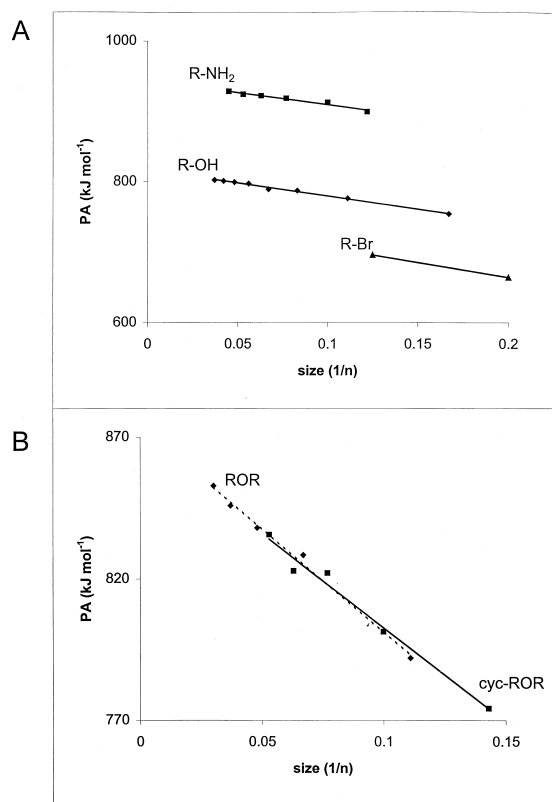


Fig. 3. Effect of size ($1/n$, where n is the number of atoms) on the proton affinity (PA) of (A) ■ n-alkylamines; ◆ alkanols; ▲ alkylbromides and (B) ◆ dialkylethers; ■ cyclic ethers.

As long ago as 1972, Aue et al. [11], showed that PA values of alkylamines correlated with their solution basicity and also that they correlated somewhat linearly with ionization energy.

Proton affinity values [12] increase along an homologous series and reach an asymptote for the largest members. However plots of PA versus $1/n$ also give excellent straight lines and these too can be used to estimate PA values for missing members. On the basis that protonation is analogous to ionization, the significance of the slope of the line should again be indicative of the extent of charge delocalization. Figure 3 shows such plots for the series CH_3NH_2 , CH_3OH , CH_3Br , ROR and cyclic ethers. Note that in Fig. 3B, two of the cyclic ethers have the same reported PA value ($\text{C}_4\text{H}_8\text{O}$, 822 kJ mol^{-1} and

$\text{C}_5\text{H}_{10}\text{O}$, 823 kJ mol^{-1} . Possibly a revision is in order.)

Two useful empirical equations relate bond dissociation energies in unsymmetric proton bound pairs $[\text{AH}^+\text{B}]$. The hydrogen bond strength, $D[\text{AH}^+\text{B}]$, is related to the PA values of the partners by the expressions

$$D[\text{AH}^+\text{B}] = 0.46[\text{PA}(\text{B}) - \text{PA}(\text{A})] + 129 \pm 8 \text{ kJ mol}^{-1}$$

In each partner here the hetero-atom is oxygen [13], and

$$D[\text{AH}^+\text{B}] = 0.26[\text{PA}(\text{B}) - \text{PA}(\text{A})] + 126 \pm 6 \text{ kJ mol}^{-1}$$

for $[\text{NH}^+\text{O}]$ pairs [14].

These equations also permit reasonable estimates to be made for $\Delta_f H$ values for ions in which the proton bridges a radical and a molecule [15].

4. Even and odd electron ions

The first systematic attempt to quantitatively correlate ion thermochemistry with simple structural variations (other than homologation) in odd and even electron ions, concerned repetitive functional group substitution at a formal charge bearing site. It was shown [16] that the $\Delta_f H^0$ value of the ion changed exponentially with the size of the ion, the latter again being represented by the number of atoms, n , in the ion, i.e., $\Delta_f H^0[\text{ion}] \propto \ln [n]$.

As can be seen in Fig. 4 this works well for the familiar series from CH_3^+ to $(\text{CH}_3)_3\text{C}^+$ and also for successive substitution of OH, OCH_3 and NH_2 in a methyl cation; note that $\text{HC}(\text{NH}_2)_2^+$ is estimated. It is important to note that for similar substitutions in many other odd electron ions and also even electron ions where the charge is localized at a multiple bond or conjugated system, the lines in the plots are, for a given substituent, essentially parallel to each other [16]. This gives greater utility to these simple correlations.

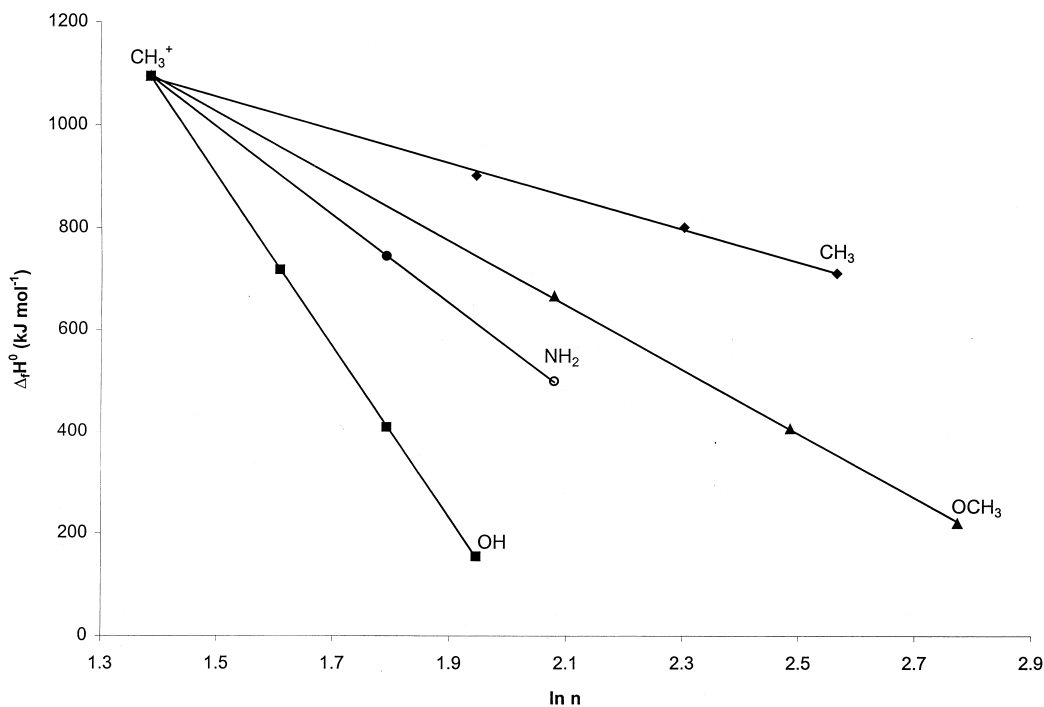


Fig. 4. $\Delta_f H^\circ$ values for sequential substitution in CH_3^+ as a function of $\ln n$: \blacklozenge CH_3 substitution; \blacktriangle OCH_3 substitution; \bullet NH_2 substitution, \circ extrapolated value; \blacksquare OH substitution.

Anomalous behavior or results can be readily seen; indeed it is always worthwhile to appraise critically both reference and new values for an ionic heat of formation by consideration of its expected value based on substituent effects.

The effect of substitution at a formal charge bearing site and adjacent to or remote from the charge is well exemplified by the data shown in Table 1 [17]. Here it can be seen clearly that the replacement of H by OH in a series of alkenes is strongly stabilizing at the double bond ($\sim 300 \text{ kJ mol}^{-1}$), whereas at other positions the stabilization in the ion is the same as for the neutral analogues.

Before leaving these general schemes, two particular ions deserve discussion. The first is $(\text{CH}_3)_2\text{C}^+\text{NH}_2$, whose $\Delta_f H^\circ$, 590 kJ mol^{-1} [3] comes principally from an appearance energy (AE) measurement for the loss of CH_3 from $(\text{CH}_3)_3\text{CNH}_2$, an apparent simple bond cleavage. However, as pointed out by Hammerum and Derrick [19], the reaction is accompanied by a flat-topped metastable peak with a

large kinetic energy release (KER) $\sim 11 \text{ kJ mol}^{-1}$ (110 meV). This indicates that the reaction has a significant reverse energy barrier and so the above $\Delta_f H^\circ$ must be an upper limit.

Table 1

Effect on $\Delta_f H^\circ[\text{ion}^+]$ of the substitution of an OH group at various position in simple olefins. ($\Delta_f H^\circ$ are given in kJ mol^{-1}).

Radical cation	$\Delta_f H^\circ$ [neutral]	$\Delta_f H^\circ$ [ion]	$\Delta(\Delta_f H^\circ)$	
			Neutral	Ion
$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	-1	929	—	—
$\text{HOCH}=\text{CHCH}_2\text{CH}_3$	-177 ^a	628	176	301
$\text{CH}_2=\text{C}(\text{OH})\text{CH}_2\text{CH}_3$	-179 ^a	628	178	301
$\text{CH}_2=\text{CHCH}(\text{OH})\text{CH}_3$	-161	756	160	166
$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OH}$	-152	770	151	159
$\text{CH}_2=\text{C}(\text{CH}_3)_2$	-18	874	—	—
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$	-160	736	142	138
$\text{HOCH}=\text{C}(\text{CH}_3)_2$	-192 ^a	607	170	267
$\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_3$	-22	896	—	—
$\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{OH}$	-172	737	150	159
$\text{CH}_2=\text{CHCH}_2\text{CH}(\text{OH})\text{CH}_3$	-188	717	166	179
$\text{CH}_2=\text{CHCH}(\text{OH})\text{CH}_2\text{CH}_3$	-182	725	160	171

^a From additivity, references 1 and 17.

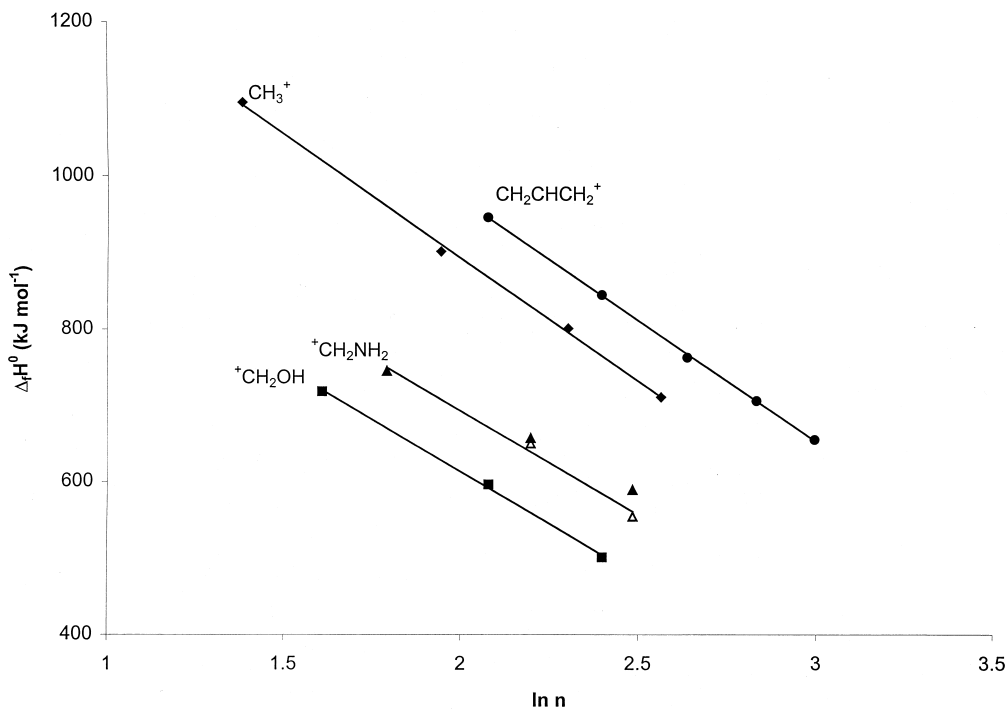


Fig. 5. Effect of sequential methyl substitution at the charge bearing site in ● CH₂CHCH₂⁺; ◆ CH₃⁺; ▲ ⁺CH₂NH₂, △ 170 revised values (see text); ■ ⁺CH₂OH.

Very recently, we have measured the AE for loss of C₂H₅ from C₂H₅C(CH₃)₂NH₂ and loss of C₂H₃ from CH₂CHC(CH₃)₂NH₂ (unpublished data). The former reaction has a very small KER value compatible with C₂H₅ loss being without a reverse energy barrier. The revised $\Delta_f H^0[(CH_3)_2C^+NH_2]$, from these two measurements, 554 kJ mol⁻¹, is shown in Fig. 5. This result is in agreement with the conclusions of Hammerum and Derrick [19], particularly that $\Delta_f H^0[(CH_3)_2C^+NH_2]$, 590 kJ mol⁻¹ [3], is likely too high. The data shown in Fig. 5, however, show that the $\Delta_f H^0[CH_3CH^+NH_2]$ is also too high to achieve a linear plot. A reassessment of the AE for CH₃CH⁺NH₂ from sec-propylamine gives a $\Delta_f H^0$ value of 650 kJ mol⁻¹ (unpublished data).

Another recently revised $\Delta_f H^0$ is that for the propanoyl cation, CH₃CH₂CO⁺. The listed $\Delta_f H^0$, 590 kJ mol⁻¹ [3], is surprisingly low, indicating an unexpected large stabilization of CH₃CO⁺ ($\Delta_f H^0 = 653$ kJ mol⁻¹ [3]) by methyl substitution therein. As analogy, consider the change in $\Delta_f H^0$ in going from

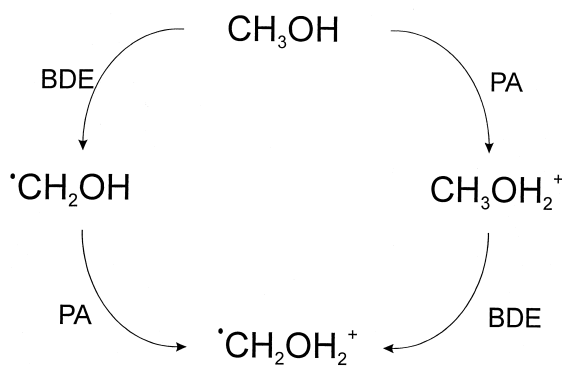
acetic to propanoic acid, $\Delta\Delta_f H^0 = -40$ kJ mol⁻¹ [3,9]. The new value for [C₂H₅CO⁺], 618 kJ mol⁻¹ [20], very closely reflects the differences for the homologous acids, $\Delta\Delta_f H^0 = -37$ kJ mol⁻¹. This too shows that additive effects accompany substitution away from the formal charge site in an ion.

5. Distonic ions

Distonic ions, i.e., radical cations in which the charge and the radical sites are formally separated, were discovered, in the early 1980s, to be quite common in the gas phase [21]. These ions are not generated by direct ionization but rather by isomerization of conventional radical cations. Because of this, experimental measurement of their $\Delta_f H^0$ is difficult (this requires the unambiguous production of a pure distonic ion). Therefore, it became important to develop a means to estimate $\Delta_f H^0$ values for these species.

As early as 1977, Benoit et al. [22] proposed an

approach allowing the $\Delta_f H^0$ of distonic ions to be evaluated. It was based on the following two assumptions: (a) that the homolytic bond strength in an *even* electron ion (a protonated species) is the same as for that for the analogous molecule and (b) that the proton affinity of a free radical is the same as that of the analogous molecule. For example, to estimate the $\Delta_f H^0[\text{CH}_2\text{OH}_2^+]$, the $\text{H}-\text{CH}_2\text{OH}_2^+$ bond strength and the proton affinity of $\cdot\text{CH}_2\text{OH}$ are assumed to be the same as that in methanol (see Scheme 1). If this is the



Scheme 1

case, then the $\Delta_f H^0$ of the distonic ion can be estimated using known thermochemical data.

However, this was later extensively tested [23] and it was concluded that the proton affinity of free radicals were in general, not the same as those of the appropriate neutral molecules, protonated at the same functional group. Likewise, hydrogen atom affinities, HA (the ionic equivalent of a homolytic bond dissociation energy) namely ΔH_r for $\text{RX}^+\text{H} \rightarrow \text{RX}^+ + \text{H}$ were generally lower than the corresponding homolytic bond strengths, by as much as 40 kJ mol^{-1} . The discrepancies were particularly severe for α -distonic ions.

This problem was reassessed in 1997 by a series of theoretical calculations [24], with particular regard to additivity-type schemes being used to estimate $\Delta_f H^0$ for distonic radical cations, where for the $\text{CH}_3\text{OH}^{+\cdot}/\text{CH}_2\text{O}^+\text{H}_2$ isomers (Scheme 1) additivity had so signally failed. For example, the PA of the $\cdot\text{CH}_2\text{OH}$ radical at oxygen is 695 kJ mol^{-1} ; for CH_3OH , it is 754 kJ mol^{-1} [12] and the bond dissociation energy $\text{D}(\text{H}-\text{CH}_2^+\text{OH}_2)$,

465 kJ mol^{-1} is far above that in CH_3OH , 400 kJ mol^{-1} . The calculations confirmed the above values, which are based on experiment, and showed that for all α -distonic ions (i.e., $\cdot\text{CH}_2\text{X}^+\text{H}$ where $\text{X} = \text{OH}, \text{NH}_2$, halogen etc) the additivity assumptions indeed fail. The calculations also demonstrated that for other distonic ions, where the charge and radical sites are separated by at least one intervening atom, the additive approach is not unreasonably in error.

6. Bond dissociation energies

The prediction of homolytic bond dissociation energies has benefited greatly from the introduction of a new electronegativity scale by Luo and Benson [25], based on the so-called covalent potential, V_x . Empirical equations using V_x have successfully been applied to a wide range of neutral systems [26], as well as to estimate additivity parameters, [27], ionization energies [28], and heats of formation [25].

Heterolytic bond strengths, $\text{D}[\text{R}^+-\text{H}^-]$, have also been considered with particular reference to ion-stabilization energy and the effect of ion size [29]. It was shown that, for example, primary, secondary and tertiary carbocation $\text{D}[\text{R}^+-\text{H}^-]$ values were each linear functions of $\ln[\text{ion size}]$, as were data for olefinic and acetylenic even electron ions. Ions containing allylic Π -systems and propargyl or allenyl ions had the same ionic stabilization, within experimental uncertainty (i.e. they were colinear). Exceptions to these simple relationships could all be ascribed to special structural features.

An alternative approach [30] to estimating heterolytic bond strengths in unsaturated organic chain compounds, $\text{D}(\text{R}^+-\text{X}^-)$ (where R^+ is an unsaturated chain cation, e.g., allylic), involved the inclusion of the covalent potential in equations having four parameters. One was to allow for the steric compression relief (resulting from the bond fission) and another to account for the stabilization and destabilization occurring in the allylic, propargylic and cyanated cations. Agreement between calculated and experimental values was very good and cases of significant disagreement could easily be rationalized. Although good

precision results from these multiparameter equations, they do not lend themselves so readily to quick application as those that can be expressed in simple graphical form.

7. Summary

Over the past 30 years a significant body of reliable experimental thermochemical data has accumulated. This has been sufficient to allow a variety of useful, simple thermochemical correlation schemes to be developed. Their great utility is to enable the researcher to estimate an unknown ionic heat of formation, proton affinity, ionization energy or heterolytic bond strength or, equally important, to critically evaluate new or existing data.

Acknowledgement

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