One electron less or one proton more: how do they differ?

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Abstract

From the NIST website and the literature, we have collected the Ionisation Energies (IE) of 3,052 and the Proton Affinities (PA) of 1,670 compounds. For 614 of these, both the IE and PA are known; this enables a study of the relationships between these quantities for a wide variety of molecules. From the IE and PA values, the hydrogen atom affinities (HA) of molecular ions M•+ may also be assessed. The PA may be equated to the heterolytic bond energy of [MH]+ and HA to the homolytic bond energy. Plots of PA versus IE for these substances show (in agreement with earlier studies) that, for many families of molecules, the slope of the ensuing line is less negative than −1, i.e. changes in the PA are significantly less than the concomitant opposite changes in IE. At one extreme (high PA, low IE) are the metals, their oxides and hydroxides, which show a slope of close to −1, at the other extreme (low PA, high IE) are the hydrogen halides, methyl halides and noble gases, which show a slope of ca. −0.3; other molecular categories show intermediate behaviour. One consequence of a slope less negative than −1 is that the changes in ionic enthalpies of the protonated species more closely follow the changes in the enthalpies of the neutral molecules compared with changes in the ion enthalpies of the corresponding radical cations. This is consistent with findings from ab initio calculations from the literature that the incoming proton, once attached to the molecule, may retain a significant amount of its charge. These collected data allow a comparison of the thermodynamic stability of protonated molecules in terms of their homolytic or heterolytic bond cleavages. Protonated nitriles are particularly stable by virtue of the very large hydrogen atom affinities of their radical cations.

KEYWORDS
protonated molecules, proton affinity, hydrogen atom affinity, ionisation energy, gas-phase ion chemistry

1 | INTRODUCTION

A great number of mass spectra have been measured, as exemplified by the huge NIST index that contains over 100,000 mass spectra. Most of these spectra have been obtained using electron ionisation. This method requires molecules to be volatile and so places significant limits on its use. Therefore in general, electron ionisation and similar ionisation methods such as photoionisation are restricted to molecules of low molecular weight. Considerable efforts have been made to develop ionisation methods for nonvolatile, thermally labile, and/or...
high molecular weight species, such as electrospray ionisation (ESI) and matrix-assisted laser desorption-ionisation (MALDI).

Electron ionisation and photoionisation usually produce radical cations and these processes can be represented as: \( M \rightarrow M^{+} + e^{-} \); the energy required for this process is the ionisation energy (IE) and the IE of a molecule \( M \) is given by:

\[
\text{IE}(M) = \Delta H^0(M^+) - \Delta H^0(M)
\]

From IE measurements, the Enthalpies of Formation of \( M^{+} \), \( \Delta_f H^0(M^{+}) \), may be assessed. ESI and MALDI usually lead to protonated species and this can be represented as: \( M + H^+ \rightarrow [MH]^+ \); the energy gained by this process is the Proton Affinity (PA) and so the PA of the molecule \( M \) is given by:

\[
\text{PA}(M) = \Delta H^0(M) + \Delta H^0(H^+) - \Delta H^0([MH]^+)
\]

where \( \Delta H^0(H^+) \) is the enthalpy of formation of a proton. From appropriate PA measurements, \( \Delta_f H^0([MH]^+) \) may be assessed. IE and PA values are positive numbers.

By inspection, equation (3) follows:

\[
\text{PA}(M) = -\text{IE}(M) + \text{IE}(H^+) + \text{HA}(M^{+})
\]

where \( \text{IE}(H^+) \) is the ionisation energy of a hydrogen atom and \( \text{HA}(M^{+}) \) is the hydrogen atom affinity of \( M^{+} \), which can be equated to the heterolytic bond dissociation energy of \( [MH]^+ \). PA can be equated to the heterolytic bond dissociation energy of \( [MH]^+ \), \( [MH]^{+} \rightarrow M + H^+ \). (Most of the molecules \( M \) studied are closed shell systems; in the case of radicals \( M^* \), the ionised form is \( M^+ \) and the protonated form becomes \( [MH]^+ \). This will be emphasized when required).

A typical energy diagram of a protonated molecule is shown in Fig. 1 which gives the energy levels for \( [MH]^+ \). \( M + H^+ \) and \( M^+ + H^+ \) relative to \( M + H^+ (=0) \); PA, IE and HA are as indicated, \( \text{IE}(H^+) = 1312 \text{ kJ/mol} \). From this figure, Eqn (3) can be derived.

\[
\text{PA}(M) = -\text{IE}(M) + \text{IE}(H^+) + \text{HA}(M^{+})
\]

The quantities IE, PA and HA as shown in Eqn (3) for a wide variety of classes of molecules, as has been done previously for other selected categories. This we have done by collecting data from the NIST database and calculating HA from Eqn (3). Our major objective was to assess the heterolytic (i.e. the PA) and homolytic (i.e. the HA) bond dissociation energies for a wide variety of protonated molecules, as indicated in Fig. 1, and to evaluate any relationships between PA and HA. Since a wealth of data is now available, we will provide an overview of the most salient features. Of particular importance for the present study are the stabilisation effects at the charge-bearing site of \( M^{+*} \) and \( [MH]^+ \). That such species can have marked different stabilities was demonstrated recently in a study of protonated \( [MH]^+ \) and ionised \( (M^{+*}) \) pyridine-substituted N-heterotriangulenes.

2 RESULTS AND DISCUSSION

2.1 Plots of PA against IE

In general, according to Eqn (3), high PA values should correspond to low IE values and vice versa. This is to be expected because a tightly bound electron in a molecule will be hard to remove and at the same time it will also be difficult to covalently attach a proton. However, the value of HA will also play a role. Previous work has shown that for many molecule categories, a plot of PA versus IE does not yield a line with slope of -1, as expected from Eqn (3) if HA does not change, but a significantly less negative slope, i.e. the changes in PA are often smaller than the concomitant opposite changes in IE. Of particular interest are methyl group substituent effects; such substitutions lead to stabilisation of the charge in both \( M^{+*} \) and \( [MH]^+ \) due to the polarisability of the methyl group. For example, Aue et al observed...
that for the series CH$_3$NH$_2$, (CH$_3$)$_2$NH and (CH$_3$)$_3$N a slope of $-0.42$ ensues, which according to Eqn (3) shows that the HA decreases in this order. Henderson et al$^{13}$ pointed out that this in turn shows that in these cases the radical cation M$^{\ast\ast}$ becomes more stabilised relative to [MH]$^{-}$ upon methyl substitution, although both M$^{\ast\ast}$ and [MH]$^{-}$ are of the same charge type. These authors conclude that stabilisation of M$^{\ast\ast}$ relative to [MH]$^{-}$ may be expressed in terms of the delocalisation of charge and spin into the methyl groups of M$^{\ast\ast}$. The above are substitutions at a charge-bearng site. In contrast, for substitution at the non-charge-bearing site, e.g. CH$_3$NH$_2$ $\rightarrow$ CH$_3$CH$_2$NH$_2$ $\rightarrow$ (CH$_3$)$_2$CHNH$_2$ $\rightarrow$ (CH$_3$)$_3$CNH$_2$, a slope of ca. $-1$ is found, see also Fig. 1 in Ref 4; in this case, the stabilisation is significantly less than in the case of substitution at a charge-bearing site, both in M$^{\ast\ast}$ and in [MH]$^{-}$; for evaluations and discussions of substitutions at charge-bearing and non-charge-bearing sites, see Refs.$^{14-22}$

From a literature survey, it appears that the above situation, namely that a plot of PA versus IE gives a line with a slope less negative than $-1$, is the rule rather than the exception. For example Ref. 5 lists the slopes for a variety of classes of compounds and, with the exception of mercaptans (slope = $-0.98$) and aromatic amines (slope = $-1.0$), they are all less negative than $-1$.

To further investigate these matters, we have collected from the NIST website (accessed on February 2017)$^{23-27}$ and from the literature the IEs of 3,052 and the PAs of 1,670 compounds. The data from the NIST website are included in the supplemental (S-1). For 614 substances both the IE and PA are known and this enables a study of the relationships between these quantities (and of HA) for a wide variety of molecule categories, ranging from metal oxides (high PA, low IE) to the hydrogen halides (low PA, high IE). The plot of PA against IE for these 614 compounds is shown in Fig. 2, where the hydrogen radical is as indicated. Also shown in this figure in grey shades are the HAs; the darker, the greater the HA. In agreement with the argument of Maksić and Vianello,$^7$ there are only 32 out of 3,052 compounds with an IE larger than that for a hydrogen radical (including the noble gases He, Ne, Ar, Kr and the molecules CF$_3$C≡N, CHF$_3$ and CO); this reduces to only 18 out of 614 for those compounds for which both IE and PA have been measured. For the corresponding protonated forms of these molecules, heterolytic cleavage requires less energy than homolytic cleavage, but they are a minority. The dotted line through H$^\ast$ represents the tipping line: to the left PA > HA, to the right PA < HA, see also Fig. 1. From Fig. 2 it can be seen that, at best, a weak correlation exists between the PA and IE. However, as shown in earlier work, much better correlations ensue when categories of molecules are compared.

The IE and PA histograms are also shown in Fig. 2 (30 bins per axis). The IE distribution appears Gaussian but the PA distribution is skewed, in that there appears a lack of high PA values; thus high PA values are less frequent than low IE values. (This is also apparent from the histogram of all 1,670 collected PA values, although in that case it could be argued that such high PA values have simply not been measured.)

We will first discuss some cases on the extremities of the plot in Fig. 2, namely, compounds with high PA and low IE on the one hand, and those with low PA and high IE on the other.

**FIGURE 2** Plot of the PA versus the IE for 614 compounds. The shade of the data points indicates the magnitude of HA as indicated. In the margins opposing the x- and y-axis, a histogram of IE and PA is plotted, respectively. The x- and y-axis are divided in 30 bins to create the histograms. Vertical dashed line indicates IE[H$^\ast$].
It appears that the metal oxides and hydroxides (Cs$_2$O, K$_2$O, Na$_2$O, Li$_2$O, SrO, CaO, CsOH, KOH and FeO) have the largest measured PAs and lowest measured IEs. A plot of PA against IE is given in Fig. 3a (in the following graphs, the PA and IE axes have the same scale). The data point for SrOH is clearly an outlier, probably because Sr in SrOH has a valency of +1; thus this data point may belong to a different family of species. It is clear that the slope of the line is close to $-1$ ($-1.17 \pm 0.05$ [95% confidence interval]). In such a situation, HA would remain relatively constant as indeed is the case, see Fig. 3b in which HA is plotted against PA. At this point it is worth noting that such PA versus IE curves as shown in Fig. 3a have predictive value: for example, the IE for NaOH is unknown, but can be estimated from its known PA, 1072 kJ/mol and from Fig. 3a, IE (NaOH) = 737 kJ/mol. Conversely, the measured IE of Rb$_2$O is 447 kJ/mol, leading to an estimated PA of 1410 kJ/mol. For MgO the NIST data base lists two values for its IE, 845 and 936 kJ/mol, but the former is more in keeping with that (808 kJ/mol) estimated from its PA (988 kJ/mol).

At slightly lower IEs are the metal atoms, see Fig. 4,28 and although the data are somewhat scattered, the slope here, too, is close to $-1$ ($-1.18 \pm 0.09$ [95% confidence interval]). At very high IE and low PA values are the noble gases. As can be seen from Fig. 5a, a plot of PA versus IE gives a shallow line, with a slope of only $-0.27$. For such a shallow line, the HA affinity decreases rapidly with PA, see Fig. 5b. This figure also shows that the heterolytic bond dissociation energy of [HeH]$^+$ is exceedingly large, 1239 kJ/mol and this has been reported previously.8 The noble gases represent an extreme case, but other classes of compounds also behave like the noble gases in this respect, such as the hydrogen halides (HX), methyl halides (CH$_3$X, X = F, Cl, Br, I) and the hydrogen chalcogenides, H$_2$Y (Y = O, S, Se, Te) for which the PA versus IE curves have slopes of $-0.26$, $-0.32$ and $-0.11$ respectively, see below.
From these extreme situations, a simple (but possibly incorrect and/or incomplete, see below) interpretation may ensue. For molecules M having large PAs, transfer of H⁺ to M may be more or less complete and the protonated molecule can be represented as M⁺H⁻. In that case, any stabilisation in M⁺H⁻ may also be present to about the same extent in M⁺⁺ and so a slope of -1 will ensue. With respect to the results of the above metals (Fig. 4), we note that calculations by Galbraith et al. on protonated metal atoms [MetH⁺] (Met = Sc, Ti, V, Cr, Mn, Co, Ni, Cu and Zn) have shown the charge on [MetH⁺] to be 90% on the metal atom and so [MetH⁺] is better represented as Met⁺⁻H⁻, rather than the proton structure MetH⁺. By contrast, for molecules of low PA, [MH⁺] may well be better represented as M⁻H⁺ where the nature of M, as far as the PA goes, is not as important as for M⁺H⁻, hence resulting in a shallow PA versus IE line.

It appears, also from the literature, that for intermediate PA and IE values, many different values for the slopes may be obtained. As mentioned above, the methyl substituent is the archetype for studying charge stabilisation effects. A charge (positive or negative) will be stabilised by a methyl substituent due to polarisation of the methyl group. Indeed, it is found that methyl substitution always leads to an increase in PA (and a decrease in IE). Celebrated cases of this effect are the amines and phosphines, XH₃, CH₃XH₂, (CH₃)₂X and (CH₃)₃X (X = N, P) and we present here the NIST data to highlight the marked difference in behaviour of these two subsets of molecules. From these extreme situations, a simple (but possibly incorrect and/or incomplete, see below) interpretation may ensue. For molecules M having large PAs, transfer of H⁺ to M may be more or less complete and the protonated molecule can be represented as M⁺H⁻. In that case, any stabilisation in M⁺H⁻ may also be present to about the same extent in M⁺⁺ and so a slope of -1 will ensue. With respect to the results of the above metals (Fig. 4), we note that calculations by Galbraith et al. on protonated metal atoms [MetH⁺] (Met = Sc, Ti, V, Cr, Mn, Co, Ni, Cu and Zn) have shown the charge on [MetH⁺] to be 90% on the metal atom and so [MetH⁺] is better represented as Met⁺⁻H⁻, rather than the proton structure MetH⁺. By contrast, for molecules of low PA, [MH⁺] may well be better represented as M⁻H⁺ where the nature of M, as far as the PA goes, is not as important as for M⁺H⁻, hence resulting in a shallow PA versus IE line.

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mentioned above, a methyl substituent always stabilises a charge and we have collected such data for CH₄, NH₃ (and PH₃), H₂O (and H₂S), HF (and HCl, HBr, HI) and present the slopes of the PA versus IE curves in Table 1. The R² values (in parentheses) are also listed except for the halides for which only two data points exist. It can be seen that the slope increases from left to right and from top to bottom. Thus for example for HF, the increase in PA for CH₃F is only ca. ⅓ of the decrease in IE and so forth. We are currently investigating the origin of these effects by ab initio charge distribution calculations.

### 2.2 | PA and HA

It has been shown above (and also in the literature) that for many categories of gaseous species an inverse relationship exists between the PA (the heterolytic bond energy) of its protonated form and the HA (the homolytic bond energy) of its ionised form. This happens when the slope of the PA versus IE line is less negative than −1, and is frequently the case. Thus, the stronger the heterolytic bond in [MH]⁺, the weaker the homolytic bond will be and vice versa. This may be referred to as a stockholder principle along the lines of Maksić and Vianello, i.e. the more investment in PA, the more profit in HA.

As has been pointed out previously, the HA is a significant property of a radical cation M⁺⁺. HA data allow the estimation of the driving force for H⁺ abstraction by an ionised functional group from a neutral H⁺ donor, for example, a C–H bond. It appears that many radical cation centres are very strong H⁺ acceptors and therefore many intramolecular (and intermolecular) transfers of a hydrogen atom from an aliphatic chain to a cation centre have little energy requirements or can even be exothermic making rearrangement reactions via distonic ions possible, for example in the McLafferty rearrangement. Thus from the NIST compilation, the HA of the 2-pentanone radical cation is 426 kJ/mol, whereas the C–H bond dissociation energy of e.g. ethane is 420 kJ/mol. Hence, the thermochemistry of isomerisation of radical cations by H⁺ (as well as H⁺) transfers can be estimated from thermochemical data. Kuck also concludes that radical cations of aliphatic nitriles have very high HAS and we agree: the largest HAS are for (in that order): Ne⁺⁺, Ne⁺⁺, SF₆⁺⁺, CF₃C≡N⁺⁺, HF⁺⁺, and HC≡N⁺⁺ with CH₃C≡N⁺⁺ and CH₃CH₂C≡N⁺⁺ on position 15 and 17 respectively (out of 614). When we order our data according to the lowest of either PA or HA, i.e. according to stability, we find at the top [HC≡NH]⁺⁺, and [CH₃C≡NH]⁺⁺ and [CH₃CH₂C≡NH]⁺⁺ at position 7 and 8, respectively. Thus, protonated nitriles are among the most stable protonated molecules.

### 2.3 | Ionic heats of formation

From the above, it appears that plots of PA versus IE are very often lines with a slope less negative than −1. This indicates that HA decreases with increasing PA,6 but it also means that, for a given category of molecules, the changes in ionic enthalpies of the protonated species more closely follow the changes in the enthalpies of the neutral molecules, compared with changes in the ion enthalpies of the

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**TABLE 1** Slopes of methyl group substitution PA versus IE curves for (sequential) methyl substitution in the parent compound. R² values in parentheses

| Compound | Slope (R²) | Compound | Slope (R²) | Compound | Slope (R²) |
|----------|------------|----------|------------|----------|------------|
| CH₄      | −0.64 (0.920) | NH₃      | −0.44 (0.997) | H₂O      | −0.40 (0.995) | HF      | −0.34 (0.992) |
| PH₃      | −1.00 (0.994) | H₂S      | −0.73 (0.995) | HCl      | −0.62 (0.995) | HBr     | −0.73  |
| HI       | −0.78      |

**FIGURE 7** Heats of formation of the neutral methyl halides, top; of the radical cations, bottom, left; of the protonated species, bottom, right.
radical cations.34 This is consistent with findings from ab initio calculations, see above, that the incoming proton, once attached to the molecule, may retain a significant amount of its charge.39-43 This effect is discussed here for the methyl halides CH3X (X = F, Cl, Br, I), but the phenomenon is general. The PA versus IE line of the methyl halides has a slope of −0.32. In Fig. 7 are shown the heats of formation of neutral CH3X (top) and the heats of formation of [CH3X]+ and [CH3XH]+ (below) on the same scale. We can see that for the radical cation there is considerable charge stabilisation due to charge dispersal when the size of the halogen atom increases. However, this effect is much less for the protonated species and the heats of formation now more closely follow those of the neutral species. (This effect also occurs markedly for the halide radical atoms X° and for the hydrogen halides HX.) This phenomenon occurs whenever the PA versus IE slope is less negative than −1, which is usually the case. This means that charge stabilisation effects can best be studied by a comparison of the heats of formation of M+° rather than of [MH]+. An extreme example is provided by the hydrogen chalcogenides, H2X (X = O, S, Se, Te). Here the slope of the PA versus IE curve is only −0.11 and thus the heats of formation of [H2X]+ almost exactly follow those of H2X. Also, HA (the homolytic bond dissociation energy, kJ/mol) falls rapidly in the order H2O° (597) > H2S° (402) > H2Se° (350) > H2Te° (306). We propose that these observations deserve additional study, for example it would be of interest to see whether H2Po, for which IE = 830 kJ/mol and for which the PA and thus HA is unknown, follows this trend. One possible rationalisation might be that for both [H2X]+ and H2X the charges on the hydrogens are similarly large, but in the absence of ab initio calculations this must remain speculative.

At this point it is appropriate to discuss the various possibilities of the magnitude of the PA versus IE slope in terms of stabilisation relative to M+°. We list the following possibilities in Table 2.

Most of the molecular categories fall in the range −1 < s < 0. We have not encountered s ≥ 0, a result that would imply no charge stabilisation and even destabilisation in [MH]+ relative to M. Of interest could be cases where s < −1. In such cases [MH]+ would be more stabilised than M+°. This may be the case to a minor extent in the metals and metal oxides for which slopes of −1.18 ± 0.09 (95% confidence interval) and −1.17 ± 0.05 (95% confidence interval) were found. For example for the protonated transition metal atoms, the structure M+° - H° may contribute to its stability, which is not possible in M+°.

### Table 2: Possible slopes of PA versus IE line and implications for stabilisation of family of ions [MH]+

| Slope (s) of PA versus IE line | Stabilisation |
|--------------------------------|---------------|
| s = −1                         | [MH]+ = M+°   |
| −1 < s < 0                     | [MH]+ < M+°   |
| s = 0                          | [MH]+ < M+° and [MH]+ = M |
| s > 0                          | [MH]+ < M+° and [MH]+ < M |
| s < −1                         | [MH]+ > M+°   |

### 2.4 Summary

A data base (NIST) mining study of the heterolytic (= proton affinity) and homolytic (= hydrogen atom affinity) bond strengths of 614 protonated species [MH]+ reveals that for many classes of closely related compounds an inverse relationship exists between these two quantities. This follows from the observation that the slopes of the lines for the proton affinity (PA) versus ionisation energy (IE) plots are very often less negative than −1, as also found previously. As a consequence, for many categories of molecules, changes in ion enthalpies of the protonated molecules follow more closely the changes in neutral enthalpies, compared with changes in enthalpies of the corresponding radical cations, formed by electron detachment. This is consistent with findings from ab initio calculations from the literature, that the incoming proton, once attached to the molecule, may retain a significant amount of its charge. An extreme example of this phenomenon is provided by the hydrogen chalcogenides, H2X (X = O, S, Se, Te). Here the slope of the PA versus IE curve is only −0.11 and thus the heats of formation of [H2X]+ almost exactly follow those of H2X. These findings deserve additional study.

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