On the Electron Affinities of Halogens and the Strength of Ionic Interactions

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A new interpretation is forwarded for the enthalpies of ionic interactions \( \Delta H_{AB} \). From observed trends in \( \Delta H_{AB} \) values for alkalisalt molecules, it is concluded that the electron affinities of halogens are in need of revision.

For an interpretation of bond strengths in simple diatomic heteronuclear molecules several empirical formalisms have been proposed. Pauling’s well known bond energy equation,

\[
\text{Fab} = IE_A + E_{AB} - EA_B
\]

whereby the bond energy is split up into ionic and covalent contributions, has led to the concept of electronegativity. The present formalism is quite interesting, although it is only formally valid to speak of bonds in the extreme case of \( X^- \), since the internuclear separation is infinite, whence, in first approximation, i.e. neglecting polarization, \( r_{AB} \approx r_A + r_B = \infty \), and correspondingly \( e^2/r_{AB} = 0 \! \). Therefore, a simple example of a completely and permanently ionic bond is the negative ion \( B^- \), which results from “bonding” between a neutral element \( B \) and a free electron \( \text{e}^- \). This has quite important consequences for the interpretation of the \( \Delta H_{AB} \) values (1) and (2) and the role of \( E_{AB} \) therein.

Indeed, \( \Delta H_{AB} \) values are now seen to represent simply the difference in energy between partly and completely ionic bonds. Although it is only formally valid to speak of bonds in the extreme case of \( X^- \), since the internuclear separation is infinite, the present formalism is quite interesting for comparisons of bonds in a particular series.

It is well known for instance that the bonds in alkalisalt molecules are largely ionic in the sense \( A^+ \! B^- \) if \( A \) is the alkali and \( B \) the halogen, whence these molecules will be used as reference-material for this investigation.

According to the new interpretation to be given to \( \Delta H_{AB} \), one should observe the following trends for alkalisalts:

1. in a given series of \( AB \) molecules wherein \( A \) is constant, \( \Delta H_{AB} (1) \) will decrease with increasing permanent polarity \( \mu \) of the \( AB \) bond. Increasing polarity in the sense \( A^+ \! B^- \) indeed means that the difference between the partly ionic bond \( AB \) and the completely ionic bond \( A^+ \! B^- \) (or in this case \( B^- \)) decreases.

2. in a given series of \( AB \) molecules wherein \( B \) is constant, \( \Delta H_{AB} (2) \) will increase with increasing permanent polarity \( \mu \) of the \( AB \) bond. Increasing polarity in the sense \( A^+ \! B^- \) now means that the actual bond \( AB \) will differ more and more from the ionic structure \( A^+ \! B^- \) (or \( A^- \)) with which it is compared.

Table 1 shows some typical examples of “experimental” \( \Delta H_{AB} \) values in order to illustrate rule 1 and 2 for, respectively, the series LiB and AF.

It is obvious that in obtaining these figures everything depends upon the accuracy of the electron af-
Table 1. $\Delta H_{AB}$ values for some ionic interactions.

<table>
<thead>
<tr>
<th>Bond $^a$</th>
<th>$\Delta H_{AB}(1)^b$</th>
<th>Bond $^a$</th>
<th>$\Delta H_{AB}(2)^b,c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiI</td>
<td>135</td>
<td>LiF</td>
<td>525</td>
</tr>
<tr>
<td>LiBr</td>
<td>147</td>
<td>NaF</td>
<td>504</td>
</tr>
<tr>
<td>LiCl</td>
<td>154</td>
<td>KF</td>
<td>508</td>
</tr>
<tr>
<td>LiF</td>
<td>181</td>
<td>RbF</td>
<td>510</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CsF</td>
<td>512</td>
</tr>
</tbody>
</table>

$^a$ Bonds arranged in order of increasing polarity.

$^b$ Values in Kcal/Mole, taken from Ref. 2 and/or from the sources given therein.

$^c$ EA values for alkali metals taken from Ref. 4 and 5.

finities. Indeed, the bond energies are known with relatively great accuracy and the knowledge of the ionization energies is not even necessary in order to get the $\Delta H_{AB}$ trends for a particular AB series.

Thus, the results in Table 1, reveal that

1. in the LiB series, $\Delta H_{AB}(1)$ increases with increasing $l$-values, completely in disagreement with rule 1 and, that

2. in the AF series (if exception is made for the LiF bond for the time being), $\Delta H_{AB}(2)$ increases with increasing $l$-values, in agreement with rule 2.

Therefore, if the arguments given above are valid, this paradoxon can only be solved by reconsidering the electron affinities of particular elements.

Recent determinations of EA values for alkali metals$^4,5$ seem to support our earlier statements about the stability of homonuclear bonds$^6$. This may be taken as a further justification for the validity of rule 2 and of our present argumentation. Hence, in view of the consistency requirements of the model, it must be concluded that the electron affinity of the halogens should be revised and that the $\Delta H_{AB}(1)$ values for alkalisalt molecules AB, as they are commonly tabulated, are mutually in-consistent with the $\Delta H_{AB}(2)$ values for the same bonds!

Refinements in the interpretation of electron affinity values in the way suggested by McMillin and Drago$^2$ for hydrogen seem interesting but have not yet been worked out. It appears from the present work that the experimentally determined EA values for halogens might be given a more differentiated interpretation too.

Extension of this procedure to other series of alkalisalt molecules would lead to similar conclusions for $EA_X$, as already obtained for $E_X$ in earlier work$^7$, on account of the relation $EA_X = E_X^3$. This consistently answers the discrepancy observed for LiF in the AF series discussed above, although even the existence of this discrepancy does not affect the conclusion concerning the revision of the EA values for halogens.

This argumentation clearly illustrates the great impact of $EA$ values for explaining chemical bonding, which is not surprising since $EA$ values describe the filling up of a singly occupied valence orbital, which is also a characteristic of ordinary chemical bonding.

Possible alterations in $EA$ values however could greatly affect relationships wherein both $EA$ and $IE$ are involved. This would be the case for the Hinze-Whitehead-Jaffé formalism for electronegativity$^8$ in the first place but also for further applications of the ionic approximation to chemical bonding such as, for instance, the interpretation of heteronuclear bond lengths$^9$.

Further investigations on these points are under way, although particular attention will be paid to Drago’s $E-C$ equation$^2$, which is a challenge for any discussion about the nature of electron-pair bond formation in general and about Pearson’s HSAB rule$^{10}$ in particular.

1. L. Pauling, J. Amer. Chem. Soc. 54, 3570 [1932].