COMMENTARY

An Analysis of the Benson–Luo Approach and Electronegativities in General

Most of the chemical reactions carried out by chemists involve enthalpies and free energies of reaction or activation in the range of 0–30 kcal mol^{-1}. The contribution to these reactions from bond energy changes fall in a similar range. For such systems, it has been possible to empirically quantify the Pauling and Mulliken electrostatic–covalent model[1] with E and C parameters.[2] Since most of these reactions involve donor–acceptor interactions, the parametrization was done for this reaction type.

The equation

$$-\Delta H = E_A E_B + C_A C_B \qquad (1)$$

provides the heterolytic bond energy component of these reactions. E_B and C_B refer to donor electrostatic and covalent bond forming properties, respectively, while E_A and C_A refer to acceptor properties. When reactions occur in polar solvents and/or involve ionic species, it becomes difficult to factor out this bonding contribution to measured thermodynamic data. Limited quantitative success is reported on simple systems.[4] For these more complicated systems the electrostatic–covalent model or the analogous polar–soft description provides qualitative rationalizations of reactivity.

When one considers enthalpies of dissociation of molecules, or the enthalpies of gas-phase ion–molecule reactions, the bond energies are usually much larger than 30 kcal mol^{-1}. For large bond energies, it has been shown[5] quantum mechanically that a transfer term has to be added to the description. Equation 2, with an electron-transfer term added, has been shown[6] to satisfactorily fit this data,

$$-\Delta H = E_{cat} E_{an} + C_A C_B + R_{an} T_{cat} \qquad (2)$$

where R refers to the receptor properties of the atom that becomes negatively charged, i.e., the animer, and T refers to transfer properties for the atom becoming positively charged, i.e., the catimer. These systems are commonly considered as a homolytic dissociation and the data is parametrized accordingly.

It is not possible to fit a wide range of bond energies to a two-term electrostatic–covalent model.[6] The transfer term must be added. Electronegativities are derived from a two-term electrostatic–covalent description of a bond and were not intended[7] to provide a quantitative fit to bond energies or chemical reactivity. They constitute an elegant way to simply predict the direction of the polarity in a bond.[7] Two major errors have been made by others. The first involves using electronegativities to correlate chemical reactivity or spectroscopy. The second involves calling other useful properties, which do not relate to the behavior of an atom in a molecule, electronegativity.

With three quantities needed quantum mechanically to describe large bond energies, how can electronegativity or any two-parameter treatment possibly work? This question has been answered[8] for a similar problem: the treatment of systems that require a two-parameter electrostatic–covalent model with one parameter. If all of the acceptors (or donors) involved in the chemistry have the same ratio of C_A/E_A (or C_B/E_B), eq 1 becomes a one donor parameter, P_B, equation. Dividing eq 1 by E_A and substituting $C_A/E_A = k$ gives

$$\frac{-\Delta H}{E_A} = E_B + kC_B \qquad (3)$$

With E_B and kC_B a function of only the base we can write

$$-\Delta H = P_B E_A \qquad (4)$$

a one-term equation where $P_B = E_B + kC_B$. It has been shown[8] that errors are made when the P_B parameters are employed to interpret chemistry where the acceptor has a different C_A/E_A ratio than that given by k. The use of a one-parameter treatment is shown to be convenient in certain circumstances,[8] but it must be used with a full realization of its limitations.

In the derivation of the Benson–Luo "electronegativity" parameters, a very similar series of aliphatic compounds R–X are used as the basis for a two-parameter treatment of a three-parameter problem. The system is further complicated by the fact that the bond dissociation energies for all the X's do not plot up linearly with the X parameters so a difference in bond energies, e.g., R–X minus CH_3–X, is utilized. This removes any disparate bonding contributions that are common to a particular X reacting with this series of R groups, for its presence in CH_3 subtracts it from the other systems. This information is thrown away in the correlation. What results is a limited correlation that will do an excellent job of predicting bond energies for R–X as long as R is an aliphatic hydrocarbon.

Sets of two-parameter treatments can be derived for any of the systems treated in eq 2 when the E_{cat}/C_A or other parameter ratios lead to a two-term equation as shown above for the one-parameter case. The resulting parameters are limited in their applicability to other systems with the same ratios. Such is the case for the Benson–Luo parameters, with the limitations being even more stringent because of the difference function utilized ($RX - CH_3X$). The parameters are not electronegativities because electronegativities are expected to apply to the entire periodic table. Furthermore, with the limited objective of the electronegativity concept, there is no need for an electro-

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negativity scale more accurate than Pauling's. It is amusing that all of these better electronegativity scales end up agreeing with Pauling's.

There is evidence in the author's reported work[9] to support the above conclusions. When the B–L parameters are used on $R_3Si–X$ compounds, the analysis fails.[9] With the exception of the fluoride derivative, the *ECT* analysis of the data provides an excellent fit.[10] The different *E*, *C*, and *T* ratios of R_3Si, compared to R, lead to the prediction[10] that the two-parameter B–L treatment cannot work for silicon if a wide range of X groups are used.

The similarity of the *E*, *C*, and *T* parameter ratios of the F, Cl, Br, and I animers[6] is worthy of note. Correlations which use only these systems (Benson and Luo not included) are very limited in their applicability. In most instances these correlations will fail when extended to most other animers, especially hydrides and carbon animers. Finally, if one wishes to derive other atomic properties, they should be given a name other than electronegativity and, more importantly, they should clearly state what their intended use is. Hopefully they will have applications that extend known qualitative trends with ionization energies. If one wishes to derive parameters that can be used to correlate and understand reactivities and spectroscopies, they must fit known bond energies.

A simple data set has been offered[6b] as a challenge to anyone proposing a new set of reactivity parameters. A matrix can be constructed consisting of rows of H, CH_3, Li, K, Cl, I, and Mn catimers versus columns of H, CH_3, Cl, I, CF_3, and CN animers. The equation and parameters for calculating bond strengths should be reported and the matrix completed by adding calculated and experimental bond energies. If this data fit is satisfactory, the *ECT* data base should be fit next. If this can be accomplished, for systems that cover the same wide range of different types of catimers and animers as in *ECT* with fewer parameters than described above, this would represent a new challenge to bonding theory.

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