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Failure of Pauling's Bond Energy Equation

By RALPH G. PEARSON

(*Department of Chemistry, Northwestern University, Evanston, Illinois* 60201)

ONE of the best known empirical relations in chemistry is Pauling's bond energy equation

$$D_{AB} = \tfrac{1}{2}(D_{AA} + D_{BB}) + 23\,(X_A - X_B)^2 \qquad (1)$$

where D_{AB}, the bond energy of an AB bond, is related to the mean of the AA and BB bond energies and the difference in electronegativities, $X_A - X_B$, of the two bonded atoms or groups.[1] The most important application of equation (1) has been to establish values of the average electronegativities (EN's) of the elements. These useful numbers can be correlated with many chemical and physical properties of the elements.[2]

If equation (1) is applied to a chemical reaction (A and C are the more metallic elements)

$$AB + CD = AD + CB \qquad (2)$$

we can immediately write the heat of the reaction in kcal. as

$$\Delta H = 46\,(X_C - X_A)\,(X_B - X_D) \qquad (3)$$

This equation makes a clear prediction which is widely taught and accepted: reaction (2) will be exothermic if the products contain the least electronegative element, A, combined with the most electronegative element, D. Pauling used equation (3) to predict the heats of various isomerizations,[3] and Hine and Weimar[4] used it to explain why carbon, compared to hydrogen, prefers to bond to the less electronegative elements such as C, S, P, and I.

The Table shows a number of experimental heats of reaction of type (2) for polar molecules, and the heats calculated from Pauling's equation (3). The equation is totally unreliable in that it gives the sign of the heat change incorrectly.

The examples chosen are gas-phase reactions. For this reason most of the data refer to halides, for which the gas-phase heats of formation are very complete.[5] It is clear from the heats of formation of solids, and from the heats of reaction in solution, that the same kind of results will be found for Group V and Group VI compounds and complexes.

Of other examples, some will agree with equation (3) and some will disagree as to the sign of ΔH. The important point is that it is possible to predict in advance when the equation will fail. Among the representative and early transition elements, electronegativity always decreases down a column in the Periodic Table. This leads to the Pauling prediction that for heavier elements in a column, the affinity for F will increase relative to that for I. The prediction is also made for preferred bonding to O compared to S, and N compared to P. The facts are always otherwise.

Consider the simple example

$$LiF(g) + CsI(g) = LiI(g) + CsF(g) \qquad (4)$$

The Pauling equation predicts that ΔH is 46 $(0{\cdot}7 - 1{\cdot}0)\,(4{\cdot}0 - 2{\cdot}5) = -21$ kcal., "because the least electronegative element, Cs, wants to bond to the most electronegative element, F." The

TABLE

Heats of gas-phase reactions at 25°

	ΔH (exp.)[a]	ΔH (calc.)[b]
$BeI_2 + SrF_2 = BeF_2 + SrI_2$	−48 kcal.	+35 kcal.
$AlI_3 + 3NaF = AlF_3 + 3NaI$	−94	+127
$HI + NaF = HF + NaI$	−32	+76
$HI + AgCl = HCl + AgI$	−25	+5
$NOI + CuF = CuI + NOF$	−10	+76
$LaF_3 + AlI_3 = AlF_3 + LaI_3$	−9	+84
$CaO + H_2S = CaS + H_2O$	−37	+25
$CS_2 + 2H_2O = CO_2 + 2H_2S$	−16	+37
$CS + PbO = PbS + CO$	−71	+64
$MeHgCl + CH_4 = Me_2Hg + HCl$	−40	+5
$MeHgCl + HI = MeHgI + HCl$	−11	+5
$COBr_2 + HgF_2 = COF_2 + HgBr_2$	−85	+66
$2CuF + CuI_2 = 2CuI + CuF_2$	−25	+14
$2TiF_2 + TiI_4 = TiF_4 + 2TiI_2$	−51	+56
$MeOH + MeOH = CH_2(OH)_2 + CH_4$	−20	+13
$CH_3F + CF_3I = CH_3I + CF_4$	−22	+69
$CH_3F + CF_3H = CH_4 + CF_4$	−19	+88

[a] Experimental heats of formation from reference 5 for halides; others from NBS Circular 500 and its revision Technical Notes 270–1 and 270–2, D. D. Wagman, *et al.*, National Bureau of Standards, Washington, D.C., Oct., 1965, May 1966. CF_3 derivatives from A. Lord, C. A. Gray and H. O. Pritchard, *J. Phys. Chem.*, 1967, **71**, 1086.

[b] Calculated from equation (3).

experimental value is +17 kcal. A rough electrostatic calculation shows that the dominant energy term is the attraction of the small Li and F atoms for each other.

Similarly, across the Periodic Table, the electronegativity of the elements increases steadily. This leads to the Pauling prediction that in a sequence such as Na, Mg, Al, Si the affinity for I will increase relative to that for F. Similarly, bonding to S and P atoms will be preferred relative to O and N. However as long as the elements have the positive group oxidation states, the facts are the opposite with very few exceptions.

Even more serious, equation (3) will almost always predict incorrectly the effect of systematic changes in A and C. For example, what happens to the heat of reaction (2) if the oxidation state of the bonding atoms change, or if the other groups attached to these atoms are changed? Such changes affect the electronegativity in a predictable way. For example, the electronegatives of Pb^{II} and Pb^{IV} are 1·87 and 2·33, respectively.[6] Similarly, the electronegativity of carbon is 2·30 in CH_3, 2·47 in CH_2Cl, and 3·29 in CF_3.[7] Increased positive oxidation state and substitution of less electronegative atoms by more electronegativity atoms always increases the electronegativity of the central bonding atom.

From equation (3), such changes again are predicted to decrease the relative affinity for F, O, and N, compared to I, S, and P. For all of the elements, except a few of the heavy post-transition elements (Hg, Tl, *etc.*[8]), the reverse is true. The impression that bonding tendencies of carbon in organic chemistry can be understood in terms of electronegativities becomes quite incorrect as soon as a range of organic radicals is considered. The more electronegative a carbon atom becomes, the *more* it prefers to bond to other electronegative atoms.

The poor results in the Table are not due to a poor choice of the electronegativity values of the elements. No reasonable adjustment of these values will improve the situation. If new parameters X_A, X_B, etc., are found for the elements to give the best fit to equation (3), they will no longer be identifiable as electronegativities. They would necessarily vary with position in the Periodic Table, with oxidation state, and with substitution effects in a way directly opposite from what one would expect of simple electronegativities.

The Principle of Hard and Soft Acids and Bases (HSAB)[9] may be used to predict the sign of ΔH for reactions such as (2). The Principle states that, to be exothermic, the hardest Lewis acid, A or C, will co-ordinate to the hardest Lewis base, B or D. The softest acid will co-ordinate to the softest base. Softness of an acceptor increases on descending a column in the Periodic Table; hardness increases on traversing the Table, for the group oxidation state; hardness increases with increasing oxidation state (except Tl, Hg, *etc.*), and as electronegative substituents are placed on the bonding atoms A or C. For donor atoms the electronegativity may be taken as a measure of the hardness of the base, donors of low electronegativity being soft. Accordingly, the HSAB Principle will correctly predict heats of reaction where the electronegativity concept fails. Some exceptions will occur since it is unlikely that any single parameter assigned to A, B, C, and D will always suffice.

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