COMMENTS

Comment on "Evaluation and Test of Pauling's Electronegativity Scale"

Derek W. Smith

Department of Chemistry, University of Waikato,
Hamilton, New Zealand

Received: June 18, 2001

Murphy et al.[1] argue convincingly and authoritatively that Pauling's electronegativity scale fails to meet fundamental requirements for acceptability. They further show that Pauling's equation,

$$D_{A-B} = {}^1/_2(D_{A-A} + D_{B-B}) + k(\Delta\chi)^2 \quad (1)$$

(where D_{A-A}, D_{B-B}, and D_{A-B} are respectively the A−A, B−B, and A−B bond energies, $\Delta\chi$ is the difference in electronegativity between A and B, and k is a constant) is valid only for a limited range of molecules where $\Delta\chi$ is small; substitution of the geometric mean $(D_{AA}D_{BB})^{1/2}$ makes little improvement. A better correlation is found if the "extra ionic energy" (EIE) is expressed as $k|\Delta\chi|$ rather than as $k(\Delta\chi)^2$, in agreement with earlier authors.[2] This obviates the difficulty of the units of χ, apparently $(\mathrm{eV})^{1/2}$ in eq 1. The purpose of this Comment is to suggest an alternative improvement of Pauling's eq 1.

I propose that the EIE can be represented by a quasi-Coulombic expression, based on the Born−Mayer equation for calculations of lattice energies in crystals,[3] so that

$$D_{A-B} = {}^1/_2(D_{A-A} + D_{B-B}) - aq_Aq_B\{1 - (\rho/r_{A-B})\}/r_{A-B} \quad (2)$$

where q_A and q_B are respectively the fractional charges on A and B, r_{A-B} is the A−B distance, and a and ρ are constants. Bratsch[4] postulated a linear dependence of χ on q

$$\chi = \chi^0(1 + q) \quad (3)$$

and equalization of the electronegativities. For a diatomic molecule AB, this leads to

$$-q_A = q_B = (\chi^0_A - \chi^0_B)/(\chi^0_A + \chi^0_B) \quad (4)$$

where the superscripts label the electronegativities of neutral atoms. (A similar expression can be derived from density functional theory, but with the sum of the hardness parameters $(\eta_A + \eta_B)$ as the denominator.[5]) A different equation applies for AB_n, but for simplicity I will use eq 4 throughout. Substitution of eq 4 into eq 2 gives an expression resembling eq 1, with the EIE proportional to $(\Delta\chi)^2$. However, the quotient in eq 4 is dimensionless, so that the problem with the units of χ inherent in eq 1 does not arise.

We can now construct a revised Pauling scale, using eqs 2 and 4. Taking the traditional Pauling values[6] of 2.1 for H and 4.0 for F as anchor points, least-squares analysis of the bond dissociation energies of the hydrogen halides and diatomic interhalogens (from the database of Murphy et al.[1]) gives electronegativities uncannily close to Pauling's for Cl, Br, and I (Table 1), with $a = 5846$ kJ mol^{-1} Å (cf. the Coulombic value of 1389 kJ mol^{-1} Å) and $\rho = 0.515$ Å (cf. 0.345 Å commonly invoked for ionic crystals[3]). The mean discrepancy between calculated and experimental dissociation energies is 3.0 kJ mol^{-1} (correlation coefficient $R = 0.999$). The magnitude of a suggests that the EIE arises from ionic-covalent resonance stabilization which, though not strictly of Coulombic origin, can be simulated by a quasi-Coulombic expression.

TABLE 1. Electronegativities χ^0 Calculated from Eqs 2 and 4[a]

H	B	C	N	O	F
2.10	1.74	2.47	3.03	3.49	**4.00**
		Si	P	S	Cl
		1.71	1.89	2.41	3.01
		Ge	As	Se	Br
		1.92	1.97	2.34	2.79
		Sn	Sb	Te	I
		1.97	1.90	2.21	2.46

[a] Values in bold type are assumed.

Electronegativities for other main group elements can be calculated from eqs 2 and 4, with the values of a and ρ obtained above, from the bond energies of AH_n or AF_n (remembering that H and F are our anchor points). For the elements in the first short period, D_{AF} for AF_n always seems to be anomalously large, presumably because of contributions from resonance structures $F^-F_{n-2}A{=}F^+$.[7] Accordingly, χ^0 values were calculated from D_{A-H} for A = B, C, N, O, and F, and from D_{A-F} for A = Si, Ge, Sn, P, As, Sb, S, Se, and Te; for the heavier, less electronegative elements, the EIEs for A−H bonds are mostly negative. All D_{A-B} were taken from the database of Murphy et al.,[1] and internuclear distances r_{A-B} from the literature.[8] Again, most of the resulting χ^0 in Table 1 are close to the traditional Pauling values. An apparent anomaly occurs with $\chi^0_{Sn} > \chi^0_{Ge}$ (although of course $\chi^0_{Ge} > \chi^0_{Si}$ is perfectly acceptable). However, the Sn−F bond energy of 414 kJ mol^{-1} in the database is of dubious provenance; if instead the Sn−Cl bond energy is used, we obtain $\chi^0_{Sn} = 1.83$. The value for χ^0_B (1.74) is surprisingly low; but if recalculated from D_{B-X} (X = halogen), admirably consistent values of 1.74, 1.71, 1.73, and 1.80 are obtained for X = F, Cl, Br, and I, respectively. Overall, the mean discrepancy $|\delta|$ between experimental and calculated D_{A-X} values (X = H, F, Cl, Br, I) for 72 bonds, including all the "anomalies", is 13.9 kJ mol^{-1} ($R = 0.954$). Doubtless, better agreement could be achieved by further refinement; however, the quantities in Table 1 fail to meet the strict criteria of Murphy et al.[1] They are to be seen as parameters that can be correlated with atomic electronegativities in electronvolts and that succeed in rationalizing much bond energy data when substituted into an intuitive, rational, and empirical expression.

I have not used data for the alkali halide or hydride molecules, which were included in the database of Murphy et al.[1] Pauling

10.1021/jp012296g CCC: \$22.00

electronegativities for the most electropositive elements have mostly been obtained from the heats of formation of crystalline halides, and not from the bond energies of gas-phase molecules. The latter are better rationalized in terms of an ionic model; the form of Pauling's equation suggests that it is appropriate only for mainly covalent bonds having smaller ionic contributions.

References and Notes

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