Hard and Soft Acids and Bases and Pauling's Electronegativity Equation

By JAMES E. HUHEEY* and ROBERT S. EVANS

(*Department of Chemistry, University of Maryland, College Park, Maryland* 20742)

Summary A modified Pauling-type calculation permits accurate estimates of bond energies of simple molecules and their partition into Madelung, covalent, and electronegativity (charge-transfer) contributions.

PEARSON[1] has shown that the electronegativity equation of Pauling:

$$\Delta = (\chi_A - \chi_B)^2 \tag{1}$$

when rearranged to consider reactions of the type:

$$AB + CD = AD + CB \tag{2}$$

to yield the enthalpy of reaction:

$$\Delta H = 46\,(\chi_C - \chi_A)(\chi_B - \chi_D) \tag{3}$$

fails to predict the correct enthalpy and often even predicts the wrong sign for ΔH. In contrast, he showed that the principle of hard and soft acids and bases (HSAB) correctly predicts the energetics *qualitatively*. We are thus presented with a paradoxical situation: the equation (eqn. 1) used to formulate the first extensive set of electronegativities seems to contradict an empirical rule (HSAB) of widespread validity. Elsewhere[2] we have examined this problem in greater detail and present here only the more important results of that work. Instead of the common concept that hard–hard interactions are stabilized solely by electrostatic interactions and soft–soft bonding is primarily covalent (with perhaps some London forces also), a somewhat different picture emerges. We believe the essence of the HSAB principle lies in the stability of the hard–hard interaction and that the so-called soft–soft interaction is merely the aggregation of the weak-bonding species "left over" when the strong-bonding "hard" species seek each other out to form the strongest bonds. The latter interaction is not merely a Madelung ("electrostatic") interaction of an ion pair, but is stabilized by strong covalent contributions as well. The presence of significant covalent energies in a molecule such as LiF has long been apparent from *ab initio* quantum-mechanical calculations.[3–5]

We have shown elsewhere[2] that the "failure" of the Pauling equation (eqn. 1) as rearranged by Pearson (eqn. 3) results from a neglect of the bond distance in combining the electronegativity energy (E_χ) with the Madelung energy (E_M) to form the "ionic resonance energy:"

$$E_\chi + E_M = \frac{-(a_B - a_A)^2}{b_A + b_B} + \frac{-(a_B - a_A)^2}{r_{AB}(b_A + b_B)^2} \tag{4}$$

where a is the inherent electronegativity,[6] b is the charge coefficient,[6] and r_{AB} is the bond distance between atoms A and B, and electronegativity equalization[6–9] is assumed.

We have used a modified Pauling approach to investigate the contribution of three terms to the total bonding energy. The first is the simple Madelung energy resulting from the coulombic attraction of partially charged atoms:

$$E_M = \frac{\delta_A \delta_B A}{r_{AB}}\,[1 - (1/n)] \tag{5}$$

where δ_A and δ_B are the partial charges on atoms A and B, A is the geometric Madelung constant, and n is the Born exponent. For integral charges, equation 5 becomes the well-known Born equation for an ion pair.

The second energy is that resulting from the transfer of electron density (δ) from the more electropositive element

Calculated charges and Madelung, covalent, and electronegativity contribution to bond energy

Molecule	δ_B	E_C	E_χ	E_M	E_T	$-\Delta H_{exp.}$	% Error	E_C/E_T
HF	−0·29	−93·5	−4·3	−21·3	−119·1	−135[a]	−11·8	0·78
	−0·38	−94·4	+6·4	−36·6	−124·6		−7·7	0·76
HCl	−0·16	−83·1	−1·2	−5·2	−89·5	−103·1[a]	−13·2	0·93
	−0·22	−83·1	+2·3	−10·1	−91·0		−11·8	0·91
HBr	−0·10	−80·3	−0·4	−1·8	−82·4	−87·4[a]	−5·7	0·97
	−0·13	−80·4	+0·6	−3·2	−83·0		−5·1	0·97
HI	−0·07	−74·0	−0·3	−0·8	−75·1	−71·4[a]	+5·1	0·98
	−0·09	−74·0	+0·1	−1·4	−75·3		+5·4	0·98
LiF	−0·62	−31·6	−32·9	−51·1	−115·5	−137·5[b]	−16·0	0·27
	−0·68	−37·3	−25·2	−62·4	−124·9		−9·2	0·30
KF	−0·67	−19·6	−39·2	−48·3	−107·2	−117·6[b]	−8·9	0·18
	−0·71	25·0	−34·3	−54·6	−113·9		−3·2	0·22
KCl	−0·80	−10·6	−14·6	−64·1	−89·3	−101·3[b]	−11·8	0·12
	−0·83	−16·5	−11·4	−68·8	−96·8		−4·5	0·17
KBr	−0·86	−7·6	−5·5	−70·0	−83·0	−90·9[b]	−8·6	0·09
	−0·86	−14·4	−4·6	−70·8	−89·7		−1·3	0·16
KI	−0·82	−8·6	−5·9	−60·7	−75·3	−76·8[b]	−1·9	0·11
	−0·84	−14·0	−2·9	−64·3	−81·3		+5·8	0·17
RbBr	−0·80	−9·5	−16·4	−58·7	−84·5	−90·4[b]	−6·5	0·11
	−0·83	−14·6	−12·9	−63·2	−90·0		+0·4	0·16
RbI	−0·77	−9·8	−15·8	−51·8	−77·4	−76·7[b]	+0·9	0·13
	−0·80	−14·3	−12·5	−56·1	−82·9		+8·0	0·17
BeF_2	−0·54	−100·8	+35·3	−171·0	−236·6	−300[c]	−21·1	0·43
	−0·64	−109·3	+92·0	−241·2	−258·4		−13·8	0·42
$BeCl_2$	−0·49	−90·7	+42·7	−123·4	−171·4	−222[c]	−22·8	0·53
	−0·62	−94·2	+100·5	−194·3	−188·0		−15·3	0·52
$BeBr_2$	−0·42	−93·6	+30·3	−85·4	−148·7	−189[c]	−21·3	0·63
	−0·54	−95·3	+77·4	−143·2	−161·2		−14·7	0·59
BeI_2	−0·36	−90·6	+17·4	−59·4	−132·6	−150[c]	−11·6	0·68
	−0·46	−92·7	+47·0	−95·3	−141·0		−6·0	0·66
MgF_2	−0·60	−71·1	+21·4	−175·5	−225·1	−254[c]	−11·4	0·32
	−0·68	−82·2	+59·8	−222·3	−244·7		−3·7	0·34
CaF_2	−0·64	−58·5	−4·8	−167·7	−231·1	−268[c]	−13·8	0·25
	−0·71	−70·4	+24·2	−203·8	−250·0		−6·7	0·28
SrF_2	−0·66	−50·4	−11·8	−167·4	−229·6	−265[c]	−13·4	0·22
	−0·72	−62·5	+12·8	−197·2	−247·0		−6·8	0·25
CH_4	+0·050	−371·1	+3·9	−6·6	−373·8	−399·2[a]	−5·9	0·99
	+0·078	−370·9	+12·5	−15·9	−374·3		−5·8	0·99
CI_4	−0·004	−265·7	0·0	0·0	−265·8	−229·6[d]	+15·8	1·00
	−0·004	−265·7	0·0	0·0	−265·8		+15·8	1·00

[a] T. L. Cottrell, "The Strengths of the Chemical Bond," 2nd edn., Butterworths, London, 1958; [b] L. Brewer and E. Brackett *Chem. Rev.*, 1961, **61**, 425; [c] L. Brewer, G. R. Somayajulu, and E. Brackett, *Chem. Rev.*, 1963, **63**, 111; [d] ref. 10.

For δ_B, E_C, E_χ, E_M, E_T, % error, and E_C/E_T, the upper value was calculated using eqn. 8 and the lower value using eqn. 9.

to the more electronegative element. It can be shown[2,7] that this energy is always stabilizing and is expressed as:

$$E = a_A\delta_A + \tfrac{1}{2}b_A\delta_A^2 + a_B\delta_B + \tfrac{1}{2}b_B\delta_B^2 \qquad (6)$$

The sum of E_M plus E_χ closely corresponds to Pauling's concept of ionic resonance energy.[10] There is one significant difference, however. Pauling assumed the covalent (or homopolar) bond energy would remain unchanged (*i.e.*, equal to the average of AA and BB bond energies) in a partially ionic bond. We have followed the more realistic approach that the *overlap* and hence the *covalent bond energy* will decrease with increasing ionicity.[11] We have tested two functions for the relation between covalent energy and partial charge.

$$E_C = E_H\,(1 - \delta^2) \qquad (7)$$

$$E_C = E_H\,(1 - \delta^2)^{\frac{1}{2}} \qquad (8)$$

where E_C is the covalent contribution to the energy of a polar bond and E_H is the expected homopolar bond energy.[10] Although equation 7 is simpler, equation 8 has a sounder theoretical basis.[11] Both give very similar results.

The total bond energy of the bond AB can be estimated as:

$$E_T = E_M + E_\chi + E_C \qquad (9)$$

To estimate the total bond energy and the appropriate charge, equation 10 may be minimized and solved for δ:[12]

$$dE_T/d\delta = d[E_M + E_\chi + E_C]/d\delta = 0 \qquad (10)$$

We have calculated total bonding energies for over fifty molecules of the halides of the non-transition elements. The correlation coefficient between our calculated energies and the experimental energies is very good ($\mathbf{r} > 0{\cdot}98$). Some typical results are shown in the Table. Unfortunately, lack of Mulliken–Jaffé electronegativity data and accurate homopolar bond energies preclude extension of this type of calculation to the transition metals at present.

Of particular interest is the partition of total energy,

E_T, into energies associated with "ionic bonding," E_M and E_χ, and "covalent bonding," E_C. The following points deserve mention:

(i) RbI, the "softest" molecule studied is also one of the most ionic (*cf.* values for δ_B and E_C/E_T, Table), contrary to the usual interpretation of HSAB interactions. The high ionicity of the molecule results from the ready ability of Rb and I to give and accept charge (because of large size) and the poor overlap of the large Rb and I atoms (and hence small covalent contributions).

(ii) LiF, a typical "hard" molecule, is predominantly ionic, but less so than NaF, KF, or RbF, and derives much of its unusual stability from *covalent* bonding. This is even more pronounced in BeF_2. "Hard–hard" interactions are thus typically *small–small* interactions that benefit from Madelung *and* covalent energies.

(iii) There are unusual trends in the experimental enthalpies of atomization, *e.g.*, $BeF_2 > MgF_2 < CaF_2 > SrF_2$. There is no obvious HSAB explanation for these values. Our values, in contrast, parallel the experimental results, and further, suggest their origin, especially the MgF_2 minimum. Beryllium fluoride (composed of two small, "hard" species) is stabilized by strong Madelung and covalent energies. Calcium and strontium fluoride benefit from relatively large Madelung energies (in spite of larger r_{AB}) because of the low metal electronegativities. Magnesium is too large to enjoy much covalent energy and too electronegative to be stabilized by charge transfer.

(iv) Electronegativity equalization, used with some success in previous electronegativity calculations,[6–9,13] can be shown to be *quantitatively inaccurate* because of neglect of E_C and E_M (which *do* tend to cancel[13]) but *qualitatively accurate* in predicting polarity.

(*Received, June 9th,* 1969; *Com.* 825.)

---

[1] R. G. Pearson, *Chem. Comm.*, 1968, 65.

[2] R. S. Evans and J. E. Huheey, *J. Inorg. Nuclear Chem.*, in the press.

[3] S. Fraga and B. J. Ransil, *J. Chem. Phys.*, 1961, **34**, 727; 1962, **36**, 1127; B. J. Ransil and J. J. Sinai, *ibid.*, 1967, **46**, 4050.

[4] A. D. McLean, *J. Chem. Phys.*, 1963, **39**, 2653.

[5] G. Doggett, *J. Chem. Soc.* (*A*), 1969, 229.

[6] All electronegativity data are from J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.* 1962, **84**, 540; J. Hinze, M. A. Whitehead, and H. H. Jaffé, *ibid.*, 1963, **85**, 148; J. Hinze and H. H. Jaffé, *J. Phys. Chem.*, 1963, **67**, 1501; *Canad. J. Chem.*, 1963, **41**, 1315, although the symbolism[7] is somewhat different.

[7] For a discussion of the symbolism used, see ref. 2, and J. E. Huheey, *J. Phys. Chem.*, 1965, **69**, 3284.

[8] R. T. Sanderson, *J. Chem. Educ.*, 1945, **31**, 2; "Chemical Periodicity," Reinhold, New York, 1960.

[9] R. P. Iczkowski and J. L. Margrave, *J. Amer. Chem. Soc.*, 1961, **83**, 3547.

[10] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N.Y., 1960, 3rd edn.

[11] See, for example, R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, 1949, **17**, 1248, and R. Ferreira, *J. Phys. Chem.*, 1964, **68**, 2240.

[12] If eqn. 8 is used to estimate E_c, δ must be obtained by an iterative procedure.

[13] J. E. Huheey, *J. Phys. Chem.*, 1966, **70**, 2086; *J. Org. Chem.*, 1966, **31**, 2365; *J. Chem. Phys.*, 1966, **45**, 405.