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The Calculation of Ionic Resonance Energies

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A molecular orbital calculation is made of the bond energy between dissimilar atoms, $A-B$. The principle of the geometric mean and experimental bond energies between similar atoms are used to evaluate the exchange integral. The other parameter needed is the difference in coulombic energy of an electron on atom A and on atom B . This is related to the difference in Pauling's empirical electronegativity values. Numerical results are given for non-polar bonds and the best polar bonds and comparison is made with experimental bond energies.

INTRODUCTION

PAULING¹ first introduced the concept of "ionic resonance energy" to account for the experimental fact that a bond between two dissimilar atoms ($A-B$) is generally stronger than could be accounted for on the basis of either the arithmetic or geometric mean of the bond strengths between similar atoms ($A-A$ and $B-B$). His explanation in terms of a resonance between ideal covalent and ideal ionic structures is open to some criticism² but his general conclusion that the extra, or stabilization energy increased with increasing polarity of the bond is undoubtedly correct. An empirical equation was proposed in which the stabilization energy is proportional to the square of the difference in electronegativities of the bonded atoms. Mulliken³ treated the problem of bonding between dissimilar atoms by a molecular orbital method and showed that Pauling's empirical equation was justified as an approximate solution to a more complex equation. The purpose of this paper is to extend Mulliken's work by some actual calculations of the "ionic resonance energies" and to compare with the values deduced from the most recent bond energies.

CALCULATIONS

The wave function for each of the two electrons in the bond $A-B$ will be represented as

$$\psi_{AB} = a\psi_A + b\psi_B \quad (1)$$

where ψ_A and ψ_B are appropriate atomic orbitals and a and b numerical coefficients. Solution of the secular equation gives for the lowest energy³

$$(1-S^2)E_1 = \frac{q_A + q_B}{2} - S\beta_{AB} + \left\{ \left(\beta_{AB} - S \left(\frac{q_A + q_B}{2} \right) \right)^2 + \frac{(q_A - q_B)^2}{4} (1-S^2) \right\}^{\frac{1}{2}} \quad (2)$$

where q , β and S have their usual meaning. If the coefficients a and b were equal in (1) then the resulting energy would be

$$(1+S)E_0 = \frac{q_A + q_B}{2} + \beta_{AB}. \quad (3)$$

The difference between E_1 and E_0 then represents the "ionic resonance energy" or the extra bond energy due to the polarity of the bond. In Pauling's terminology it would be due to the contribution of the ionic structure $A-B^+$ (assuming A more electronegative than B). If the usual convention of neglecting the overlap integral S is followed (we shall consider the validity of this later) Eqs. (2) and (3) simplify considerably,

$$E_1 = \frac{q_A + q_B}{2} + \left\{ \frac{(q_A - q_B)^2}{4} + \beta_{AB}^2 \right\}^{\frac{1}{2}} \quad (4)$$

$$E_0 = \frac{q_A + q_B}{2} + \beta_{AB}. \quad (5)$$

It can readily be seen that $E_1 - E_0$ will always be a positive quantity in terms of β (corresponding to a negative energy since q and β are negative). To calculate bonding energies we must evaluate the quantities β_{AB} and $(q_A - q_B)$, the exchange integral and the difference in the coulombic energies of an electron on atoms A and B . The absolute values of q_A and q_B are not needed since they cancel in the calculation of the energy of formation of the bonded atoms from the separated atoms. For β_{AB} we shall make the reasonable assumption that it can be represented as the geometric mean of β_{AA} and β_{BB} .⁴

$$\beta_{AB} = (\beta_{AA}\beta_{BB})^{\frac{1}{2}} = \frac{1}{2}(E_{A_2}E_{B_2})^{\frac{1}{2}} \quad (6)$$

where E_{A_2} is the bond energy of $A-A$ etc. For $q_A - q_B$ we shall follow Mulliken^{3,5} and assume that this difference is equal to the difference between the term values for the separated atoms with the conditions that the separated atoms be maintained in the same valence state as for the equilibrium distance and that both electrons of the bond circulate over both nuclei. This leads to the approximation:

$$q_A - q_B = (I_A + E_A)/2 - (I_B + E_B)/2, \quad (7)$$

¹ See L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), Chapter II for a complete discussion.

² A. Burawoy, *Trans. Faraday Soc.* **39**, 79 (1943).

³ R. S. Mulliken, *J. Chem. Phys.* **3**, 573 (1935).

⁴ L. Pauling and J. Sherman, *J. Am. Chem. Soc.* **59**, 1450 (1937).

⁵ R. S. Mulliken, *J. Chem. Phys.* **2**, 782 (1934).

where I refers to the ionization potential and E to the electron affinity for the atom in the appropriate state. The corrections for the state to be used in the calculations become involved for the polyvalent atoms but Mulliken has shown that, for the cases where calculations can be made, there is a close correspondence between the function $(I+E)/2$ and Pauling's empirical electronegativity function. Thus, expressing the energies in kcal.,

$$(I_A + E_A)/2 - (I_B + E_B)/2 = 65(X_A - X_B) \quad (8)$$

where X_A refers to Pauling's electronegativity value for

TABLE I. Bond energies for dissimilar atoms.*

Bond	$-2\beta_{AB}$	$-\beta\left(4 + \frac{(X_A - X_B)^2(65)^2}{\beta^2}\right)^{\frac{1}{2}}$	E_{AB} (Experimental)
H-Cl	77 kcal.	97 kcal.	103 kcal.
Br-Cl	51	53	53
I-Cl	45	59	50
O-Cl	44	55	49
C-Cl	68	76	78
Si-Cl	51	93	90
Ge-Cl	44	95	100
P-Cl	50	77	76
As-Cl	44	78	70
S-Cl	56	65	65
Li-Cl	39	136	119
Na-Cl	32	140	98
K-Cl	26	145	101
Rb-Cl	25	145	101
Cs-Cl	24	151	103
N-Cl	46	46	46
Si-O	39	117	103
C-O	52	83	80
N-O	35	48	52
C-S	66	66	62
C-N	54	63	66
I-Br	41	49	43
C-Br	61	64	67
P-Br	45	64	62
N-Br	41	43	45
C-H	91	95	98
N-H	62	85	93
O-H	60	109	110
S-H	75	79	83
P-H	68	68	76
As-H	59	59	57
Si-H	68	71	76
Li-H	52	88	58
Na-H	43	89	47
K-H	35	92	43
Rb-H	34	91	39
As-Br	40	66	58
Si-Br	46	80	76
Li-Br	35	122	105
Na-Br	29	127	88
K-Br	23	132	91
Rb-Br	23	132	91
P-I	40	44	42
As-I	35	44	43
C-I	54	54	52
Na-I	25	101	72
K-I	21	106	76
Rb-I	20	106	76
Cs-I	19	112	78

* The sources of these bond energies are Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (Chapman and Hall, London, 1947); Skinner, *Trans. Far. Soc.* 41, 645 (1945) and Pitzer, *J. Am. Chem. Soc.* 70, 2140 (1948). The carbon-iodine value is from Butler and Polanyi, *Trans. Far. Soc.* 39, 19 (1943). Generally only bond energies on which there is agreement to two or three kilocalories by the several sources are used in the tables. In several cases where one author's value was selected, care was taken to insure internal consistency with all bonds involving that element.

atom A etc. We shall accordingly use the X values given by Pauling¹ for all calculations of $q_A - q_B$.

Table I shows the results of the calculations made. The quantity $-2\beta_{AB}$ is the bond energy of a pure covalent bond ($a=b$ in Eq. (1)),

$$-\beta\{4 + [(X_A - X_B)^2(65)^2/\beta^2]\}^{\frac{1}{2}}$$

is the bond energy of the best polar bond, and E_{AB} is the experimental bond energy. Table II gives the experimental values of the single bond energies between similar atoms and the electronegativity values used.

Next let us consider the effect of including the overlap integral which was neglected in the preceding calculations. If we define the new quantity

$$\beta_{AB}^* = \beta_{AB} - S \left(\frac{q_A + q_B}{2} \right), \quad (9)$$

then Eqs. (2) and (3) become

$$E_1 = \frac{q_A + q_B}{2} + \frac{S\beta_{AB}^* + \{\beta_{AB}^{2*} + [(q_A - q_B)^2/4](1 - S^2)\}^{\frac{1}{2}}}{1 - S^2} \quad (10)$$

$$E_0 = \frac{q_A + q_B}{2} + \frac{\beta_{AB}^*}{1 + S}. \quad (11)$$

If the value of S is known, the β_{AA}^* and β_{BB}^* can be calculated from known bond energies between similar bonds as before. The use of the geometric mean for the evaluation of β_{AB}^* leads to some difficulty, but if the principle of the arithmetic mean is used, and if a constant value of S is assumed, then it follows that

$$\beta_{AB} = \frac{\beta_{AA} + \beta_{BB}}{2} \quad (12)$$

$$\beta_{AB}^* = \frac{\beta_{AA}^* + \beta_{BB}^*}{2} = \frac{E_{AA} + E_{BB}}{4}(1 + S), \quad (13)$$

which should be a fair approximation for bonds between atoms whose values of β are not too different.

Some calculations were made in this way of the bond energy of HCl with S equal to 0.0, 0.5 and 0.8. The corresponding energies are 100, 96 and 92 kcal. Similar results are obtained with other bonds. Evidently the bond energies are not sensitive to the value of S used, providing that a constant value can be used throughout. This is similar to the results of Wheland⁶ who investigated the effect of the overlap integral on calculated resonance energies of aromatic compounds. The general conclusions drawn may not be true, of course, for bonds between atoms of quite different values of β and hence of the overlap integral.

⁶ G. W. Wheland, *J. Am. Chem. Soc.* 63, 2025 (1941).

TABLE II. Bond energies for similar atoms.*

Element	Single bond energy	Electronegativity (X)
Hydrogen	104 kcal.	2.1
Chlorine	57	3.0
Bromine	46	2.8
Iodine	36	2.4
Lithium	26	1.0
Sodium	18	0.9
Potassium	12	0.8
Rubidium	11	0.8
Cesium	10	0.7
Phosphorous	44	2.1
Arsenic	34	2.0
Sulfur	54	2.5
Carbon	80	2.5
Oxygen	34	3.5
Nitrogen	37	3.0
Silicon	45	1.8
Germanium	34	1.7

* From the same sources as Table I.

DISCUSSION

Considering the crudities of the approximations used, the results in Table I are encouraging. It must be remembered that the comparison is to be made between experimental values of the bond energies and the values in the third column compared to the second column. Those cases where the agreement is poor are readily understandable. They are bonds which are highly polar and essentially ionic in nature. The calculated bond energies are always in excess of the observed. Now for such bonds the electronegativities used are not very good because the piling up of the electrons on the more negative atom will reduce the electronegativity of that atom and increase the electronegativity of the more positive atom. Hence the real difference in electronegativity becomes less and the "ionic resonance energy" is correspondingly reduced. For example, to give agreement with experiment in the case of sodium chloride, the X value of chlorine should be reduced by 0.35 unit and the X value of sodium increased by the same amount.

The difficulty really lies in the approximation of using one-half of the ionization potential and one-half

the electron affinity to represent the term value of an electron on a combined atom. Actually the weight to be given to each quantity should depend on the parity of the bond. For a highly positive atom the electron affinity will be of little importance because the probability of finding both electrons simultaneously on that atom is very small. For a highly negative atom the electron affinity will be of great importance because both electrons will be on that atom most of the time. The effect is clearly shown in the alkali hydrides. Hydrogen, which has a small electron affinity is forced to be highly negative in these compounds. Hence the true binding energy is much less than that calculated by Eq. (4) and in fact approaches the bond energy that would result if X_A was equal to X_B . Evidently the electronegativity value to be used for hydrogen in the hydrides is less than that used for the hydrogen in, say, hydrogen chloride.

The empirical equation developed by Pauling¹ for the "ionic resonance energy" is an expansion of Eq. (4) as was pointed out by Mulliken.³ It corresponds to an average value of β equal to -46 kcal. This is somewhat larger than the values of β deduced from Table II (about -20 kcal.). The effect is to make the empirical equation fit the data over a wider range of electronegativity differences. Actually the energies calculated from the simplified equation and the more complete expression do not differ appreciably, the more complete equation being better for small electronegativity differences and the empirical equation being better for large electronegativity differences. Since Pauling's X values were originally derived from experimental "ionic resonance energies" it might appear illegitimate to use them now to calculate the same quantities. It is our purpose here to justify the substitution of electronegativity differences for differences in coulombic energies as given by Eqs. (7) and (8). One possible advantage of the more complete treatment developed here would be in its application to calculations of resonance energies and electronic distributions of systems involving more than one kind of atom.