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Calculation of Bond Energies in Diatomic Molecules*

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An extrapolation method is proposed for an approximative evaluation of covalent bonding powers of some elements from their electronegativity values. Using these values in the bond energy equation, obtained from the principle of electronegativity equalization [3], bond energies can be calculated with an accuracy, comparable with the one, obtained by Evans and Huheey [1], who included an electrostatic attraction energy term in the calculation of bond energies. Alterations in the covalent bonding power (electronegativity) of some elements in function of the nature of the bonding partner are demonstrated. The disagreement between the Pauling and Pearson rules for the description of heteropolar bond stability is discussed.

Für eine angenäherte Berechnung der kovalenten Bindungsstärke einiger Elemente aus ihren Elektronegativitätswerten wird eine Extrapolationsmethode vorgeschlagen. Wenn man die so gewonnenen Werte in die Gleichung der Bindungsenergie einsetzt, die aus dem Prinzip der Gleichsetzung der Elektronegativitäten [3] gewonnen wurde, so können Bindungsenergien mit einer Genauigkeit berechnet werden, die mit derjenigen der Ergebnisse von Evans u. Huheey [1] vergleichbar ist, wobei von diesen Autoren ein Term für elektrostatische Anziehung bei den Berechnungen der Bindungsenergien berücksichtigt wurde. Die Änderungen in der kovalenten Bindungsstärke (Elektronegativität) werden für einige Elemente in Abhängigkeit von der Art ihrer Bindungspartner dargestellt. Der Unterschied zwischen den Regeln von Pauling u. Pearson für die Beschreibung der Stabilität heteropolarer Bindungen wird berücksichtigt.

Méthode d'extrapolation pour évaluer approximativement le pouvoir de liaison covalente de certains éléments à partir de leur électronégativité. En utilisant ces valeurs dans l'équation d'énergie de liaison, obtenue à partir du principe d'uniformisation de l'électronégativité [3], les énergies de liaison peuvent être calculées avec une précision comparable à celle obtenue par Evans et Huheey [1], qui introduisaient un terme d'attraction électrostatique dans leur calcul. Des variations du pouvoir de liaison covalente (électronégativité) de certains éléments en fonction du partenaire sont mises en évidence. On discute le désaccord entre les règles de Pauling et de Pearson pour la description de la stabilité de la liaison hétéropolaire.

1. Introduction

Recently, Evans and Huheey [1] proposed a three term function for the calculation of the bonding energy E_{AB} of the heteropolar AB bond. Apart from an electronegativity energy term and a covalent energy term, an electrostatic attraction energy term (Madelung energy) was introduced to account, in first instance, for some deviations from experimental data found by the application of Pauling's rule [14] for the calculation of heats of reaction. The failure of the latter rule in several cases was first extensively discussed by Pearson [28] whereby he referred to the "hard and soft acid-base interactions" rule, which is believed to describe these experimental data better than Pauling's original equation for the extra ionic resonance energy.

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* Taken in part from Ref. [15].

For the process $AB \rightarrow A + B$, several bond energy calculations are based upon the introduction of a similar electrostatic attraction term in the bond energy function [2]. Energy calculations for the process $AB \rightarrow A^+ + B^-$ are usually based upon electrostatic attraction forces alone [23], although it was pointed out by Pearson and Gray [33] that the inclusion of a covalent term in the bond energy function for this process leads to better results than with electrostatic equations (including polarization effects [23]) only.

In a previous paper [3] however, a formula for the bond energy was proposed, containing ionic and covalent energy terms only. It is the purpose of this paper to show that this simple formula represents experimental data for diatomic molecules as well as the Evans-Huheey formula [1], wherefrom a discussion of the discrepancy between Pauling's and Pearson's rule, cited above, can be made.

2. Theory and Discussion

The relation for the bond energy E_{AB} is given by [3]:

$$E_{AB} = (-D_{AB}) = (1/2)\,e(\chi_A + \chi_B)\,(1 + I^2)\,, \tag{1}$$

where D_{AB} stands for the dissociation energy of the AB bond, χ_X for the electronegativity of atom X (a boundary potential [3]) and I for the charge separation in the AB bond, given by the relation:

$$I = (\chi_B - \chi_A)/(\chi_A + \chi_B)\,. \tag{2}$$

It was shown that the quantity $e\chi_X$ represents not only the Coulomb integral α_X of atom X, in accordance with several authors [4–9], but also the resonance integral of the homopolar XX bond, β_{XX}:

$$e\chi_X = \alpha_X = 2\beta_{XX} \tag{3}$$

and correspondingly

$$e\chi_X = E_{XX} = (-D_{XX})\,. \tag{4}$$

Eq. (1) is then transformed into:

$$E_{AB} = (1/2)\,(E_{AA} + E_{BB})\,(1 + I^2)\,, \tag{5}$$

wherein I is now defined as:

$$I = (E_{BB} - E_{AA})/(E_{AA} + E_{BB})\,. \tag{6}$$

The heteropolar bond energy E_{AB} is seen to be given by a function of the homopolar bond energies E_{AA} and E_{BB} only. From these equations, the Pauling definition of electronegativity could be deduced in first approximation [3].

It can be shown [15] that relations (1) and (5) are formally the same as the bond energy function used by Klopman [4], although the elaboration of the formulae, especially the evaluation of the covalent bond energy term, is carried out in completely different a way.

E_{AB} could indeed be calculated with the aid of Eq. (5), provided that E_{AA} and E_{BB}, the covalent bonding powers of atoms A and B, are known. In some cases, these bonding powers E_{XX} are given by the experimental E_{XX} values.

However, it is well known that, in some interesting cases as halogens, nitrogen and oxygen f.i., the covalent bonding power E_{XX}, as it is available from the experimental dissociation energy of the XX bond, is influenced by the nature of the bonding partner [1, 10, 11, 24]. The presence of lone electron pairs in the valence shell of both the bonding partners, as discussed by Pauling [14], Mulliken [26] and Pitzer [27], is known to be one of the major causes for the experimental E_{XX} values to be lower than expected, as frequently shown in the extreme case of the fluorine molecule [12–14]. Obviously, repulsion between lone electron pairs (non-bonding effects) is of a totally different nature than covalent bonding power only. Therefore, in these cases, the experimental E_{XX} values certainly do not reflect the true bonding powers of the elements cited above.

Since covalent bonding power E_{XX} represents orbital electronegativity $e\chi_X$ of the neutral atom X and since χ_X was shown [3] to be proportional with the usual electronegativity values, given by Pauling [14], Mulliken [29] and Gordy [30] f.i., we might proceed to find the corresponding E_{XX} values for halogens in the following way:

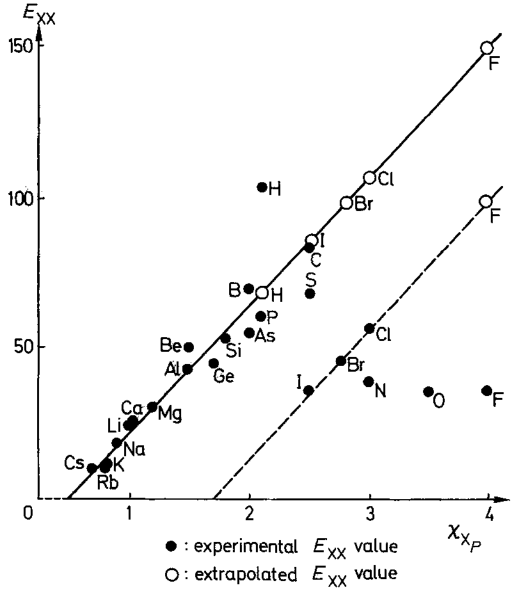

Fig. 1. The correlation between covalent bond energy values E_{XX} and the Pauling electronegativity values χ_{X_P}

Table 1. *Covalent bond energy E_{XX} and Pauling χ_{X_P} values*

Element	χ_{X_P} [14]	E_{XX} [1]
H	2.1	104
Li	1.0	26
C	2.5	83
N	3.0	39
O	3.5	36
F	4.0	36
Na	0.9	18
Si	1.8	53
P	2.1	60
Cl	3.0	58
K	0.8	12
Ge	1.7	45
As	2.0	55
Br	2.8	46
Rb	0.8	11
I	2.5	36
Cs	0.7	10
Be	1.5	51[a]
B	2.0	70
Mg	1.2	31[a]
Al	1.5	43
Ca	1.0	25[a]
S	2.5	67

[a] E_{XX} values estimated by Evans and Huheey [1], through an extrapolation procedure.

Table 2. *Extrapolated* E_{XX} *values for* F, Cl, Br, I *and* H

Element	χ_{X_P}	$E_{XX_{\text{extrapol.}}}$
F	4.0	149.5
Cl	3.0	106.5
Br	2.8	98.0
I	2.5	85.0
H	2.1	68.5

When there are no lone electron pairs in the valence shell of atoms X, the relation (4) is valid. This is shown in Fig. 1, where the experimental E_{XX} values are plotted against χ_{X_P} values, the latter being used as a measure for χ_X (all values taken from Table 1).

For elements of Group I-IV the relatively small deviations from the straight line are mainly arising from errors in electronegativity values χ_{X_P}, rather than from minor uncertainties in some E_{XX} values.

For halogens, nitrogen and oxygen (less for sulphur) however, drastic deviations are found to be attributed to the repulsion forces discussed above.

Hence, more suited values for the real covalent bonding powers of the latter elements might be obtained by the extrapolation procedure, given in Fig. 1. In this way, we try to get a correction upon $E_{XX_{\text{exp}}}$ for the presence of repulsive forces in XX bonds. But, since χ_{X_P} values are "mean" electronegativity values [14], as demonstrated in detail by Bykov [25] for χ_{F_P}, this extrapolation procedure will correspondingly lead to mean E_{XX} values for these elements X.

These extrapolated E_{XX} values are collected in Table 2. They reflect the disappearance of destabilizing effects of the above mentionned kind and will have to be used in cases, where such an element X is bonded to an element, that does not carry any lone electron pair in its valence shell, as similarly indicated by Evans and Huheey [1].

Analogous to the extrapolation methods used by other authors [1, 13, 14], an extrapolated value of about 100 kcal/mole is obtained for E_{FF} relative to the E_{XX} values of the other halogens. But the actual situation in interhalogen bonds will be more complicated than in the alkalimetal-halogen bonds f.i., since in the former bonds both the bonding partners do carry lone electron pairs in their valence shell. The evaluation of mutual interaction in heteronuclear bonds of this type is only possible, as long as we disregard interhalogen bonds containing fluorine. In these bonds, E_{FF} will decrease in comparison with E_{FF} in alkalimetal-fluorine bonds f.i. (see Fig. 1), but, at the same time, the presence of a fluorine atom will not leave the E_{XX} value of the other halogen unaffected. This is clearly shown in the FF bond itself, where E_{FF} is experimentally found to be equal to 37.5 kcal/mole.

From Fig. 1 it is also seen that the hydrogen molecule is extra stabilized in comparison with the covalent bonds of the other elements. As we can assume that χ_H is likely to be in the neighbourhood of 2.1 in the Pauling scale, an extrapolated value of 68.5 kcal/mole is deduced for the covalent bonding power of hydrogen towards other elements, in sufficient agreement with the value of about 70 kcal/mole

Table 3. *Experimental and calculated E_{AB} values*

Molecule AB	$-E_{AB_{calc.}}$	$-E_{AB_{calc.}}$[1]	$-E_{AB_{exp.}}$ [a]	Δ (%)	Δ (%)[1]
1. HF	122.4	119.1	135.0	− 9.4	−11.8
2. HCl	91.6	89.5	103.1	−11.1	−13.2
3. HBr	85.9	82.4	87.4	− 1.7	− 5.7
4. HI	77.6	75.1	71.4	+ 8.7	+ 5.1
5. LiF	132.1	115.5	137.5	− 3.9	−16.0
6. LiCl	91.3	93.4	111.9	−18.3	−16.6
7. LiBr	83.4	83.8	100.2	−16.7	−16.4
8. LiI	71.6	75.9	84.6	−15.4	−10.2
9. LiH	57.0	74.6	58.0	− 1.8	+28.6
10. NaF	135.4	112.3	114.0	+18.7	− 1.5
11. NaCl	93.7	90.5	97.5	− 3.9	− 7.1
12. NaBr	85.6	82.0	86.7	− 1.3	− 5.4
13. NaI	73.3	74.0	72.7	+ 0.8	+ 1.8
14. NaH	58.0	68.1	48.2	+23.4	+45.1
15. KF	139.3	107.2	117.6	+18.4	− 8.9
16. KCl	97.0	89.3	101.3	− 4.3	−11.8
17. KBr	88.6	83.0	90.9	− 2.5	− 8.6
18. KI	76.0	75.3	76.8	− 1.0	− 1.9
19. KH	60.1	61.1	43.6	+39.7	+42.1
20. RbF	138.0	109.1	116.1	+18.8	− 6.0
21. RbCl	97.6	91.3	100.7	− 3.1	− 9.3
22. RbBr	89.2	84.5	90.4	− 1.3	− 6.5
23. RbI	76.5	77.4	76.7	− 0.2	+ 0.9
24. RbH	60.5	63.4	39.6	+55.2	+62.6
25. CsF	140.7	—	121.0	+15.9	—
26. CsCl	98.2	—	101.0	− 2.0	—
27. CsBr	89.9	—	90.0	− 0.2	—
28. CsI	77.1	—	75.5	+ 2.1	—
29. CsH	61.0	—	42.0	+45.3	—

[a] Values in kcal/mole, taken from Ref. [1] and [17].

calculated with Eq. (7) (see below). Hence, we will tentatively use this extrapolated value for the calculation of bond energies E_{HB} and see if the results obtained are consistent with those obtained for other elements.

Results for our calculation of E_{AB} values for 29 heteropolar AB bonds are collected in Table 3, where also the E^1_{AB} values, calculated by Evans and Huheey [1], and corresponding deviations Δ from the experimental values are tabulated.

In general, the results obtained by our relatively crude appraoch remarkably parallel those obtained by Evans and Huheey [1] (except for LiH and AF bonds), although we did not take into account an explicit electrostatic energy term in the bond energy function.

Therefore, these results tend to disprove in part the suggestion of the latter authors that the introduction of a Madelung energy term in Pauling's equation for the extra ionic resonance energy is necessary [1] to obtain better agreement with several experimental data. It is now seen that a more correct (but still Pauling-like) formulation of the covalent and ionic contributions to the bond energy in the whole region $0 \leqq I \leqq 1$, especially with the use of more absolute electronegativity values E_{XX}, can account quite well for the experimental bond stability values, given in Table 3, and, hence, for the failure of Pauling's original bond energy equation for bonds which are known to be largely ionic, a failure extensively discussed by Pearson [28] and Ferreira [31].

Nevertheless, there remain some drastic deviations between calculated and experimental E_{AB} values, especially for LiX and AH bonds, as can be seen from Table 3.

As pointed out above, the extrapolation procedure yields an E_{XX} value for halogens, the validity of which is obviously depending upon the correctness of the corresponding χ_{X_P} value. Bykov [25] has shown that a constant value for χ_{F_P} f.i. is hardly to justify, since he calculated χ_{F_P} values ranging from 2.9 to 5, with a mean value of 3.5, considerably lower than the Pauling electronegativity value for fluorine (4.0).

Since electronegativity values are usually intended to give us a first (relatively crude) idea about the character of chemical bonds, the deviations Δ, found in Table 3, might provide further evidence for the variation of an element's electronegativity value in function of the nature of its bonding partner.

This can be demonstrated by a reverse argumentation, based upon Eq. (5).

Assuming again that, in first approximation, the experimental E_{AA} value represents the covalent bonding power (electronegativity) of element A fairly well, the covalent bonding power (electronegativity) E_{BB} of element B can be calculated directly from another form of Eq. (5), i.e.

$$E_{BB} = (1/2) \cdot E_{AB} + (1/2)\,(E_{AB}^2 + 4E_{AA} \cdot E_{AB} - 4E_{AA}^2)^{1/2}\,. \tag{7}$$

The E_{BB} values thus obtained from experimental E_{AA} and E_{AB} values only, are collected in Table 4. When plotted against χ_{B_P} values, they would yield Fig. 1 in first instance, and therefore, basicly support the sequence found in Pauling electronegativity values.

A detailed comparison of the deviations Δ, collected in Table 3, with the differences between the E_{BB} values obtained with the extrapolation method (Table 2) and with the aid of Eq. (7) (Table 4) for each AB bond under consideration shows that the origin of these deviations Δ just lies in the fact that, in general, the E_{XX} value of an element X (X:halogen and H) is influenced by the nature of

Table 4. *Covalent bonding power E_{BB}, calculated from experimental E_{AB} and E_{AA} values*

Molecule AB	$-E_{BB\,(\mathrm{kcal/mole})}$				
	B = F	B = Cl	B = Br	B = I	B = H
HB	163	123	100	74	—
LiB	156	129	117	100	70
NaB	128	110	99	85	56
KB	128	111	100	86	50
RbB	125	110	99	85	46
CsB	129	109	99	83	49

its bonding partner, consistent with the special case of fluorine, studied by Bykov [25].

Indeed, it follows from Table 4, that the E_{BB} values (B: halogen) in LiB bonds are about 15% higher than in the corresponding Na, K, Rb, and Cs bonds to B. In the former, the values found with Eq. (7) exceed those obtained with the extrapolation method. In the latter, only the E_{FF} value is seen to be smaller than that obtained by extrapolation, in agreement with the Δ values shown in Table 3.

The E_{HH} values follow the same trend as E_{FF}, since in LiH, E_{HH} is 25 à 30% higher than in the NaH, KH, RbH and CsH bonds. Moreover, the value of E_{HH} for these alkali-hydride molecules, i.e. in the range 50 to 70 kcal/mole, is plausible with the mean value obtained by extrapolation and might help to explain the negative values for the extra ionic resonance energy in these bonds, as found by Pauling [14].

In hydrogen halides HX, the E_{FF} value is consistent with that found for the LiF bond, but the covalent bonding powers of Cl, Br and I seem to reflect the influence of polarization effects. But these values can only be calculated by assuming E_{HH} in these bonds to be constant and equal to 68.5 kcal/mole (see above), which, in view of the results for E_{HH} obtained in alkalimetal hydride molecules, can only be valid in first approximation.

Nevertheless, in bonds of all halogens and hydrogen to Na, K, Rb and Cs, the covalent bonding powers E_{BB} are practicly constant and these values are in reasonable agreement with their usual electronegativity values, especially when the Bykov value for χ_{F_P}, i.e. 3.5, is used, corresponding to E_{FF} equal to 128 kcal/mole.

The variation of E_{BB} when going from HB and LiB bonds to the bonds of the other alkalimetals to B could be ascribed to alterations in hybridizational features, affecting electronegativity values [29, 32], polarization effects or further electron pair repulsions, although a definite description of the latter effects upon the covalent bonding power of the bonding partner is very hard to put upon a quantitative basis. But, a calculation of heats of reaction, based upon Pauling's original equation and taking into account this variation in electronegativity values, will lead to results resembling more to those predicted by Pearson's HSAB-rule than does a calculation using constant electronegativity values [28]. Just in reactions involving Li (and H)-halides and other alkalimetalhalides, the latter calculation was shown to lead to very erroneous results [1, 28].

Finally, a verification of the covalent bonding powers, which (except for H) are either determined experimentally or calculated by means of Eq. (7), can be obtained by substituting them in the expression (6) for I, the charge separation in the AB bond, wherefrom electric dipole moments can be calculated.

Results of these calculations are shown in Table 5. The agreement between calculated and experimental values is rather good, supporting the E_{BB} values, collected in Table 4. It should be emphazised that these I-values are consistent with the presence of a relatively large covalent contribution to the bonding energy, whereas the calculations made by Rittner [23] f.i. uncorrectly disregards this contribution [33]. Also, a close similarity is reached at with Klopman's results [4], although the treatment presented herein is much simplier and is based upon an

Table 5. *Experimental and calculated electrical dipole moment values*

Molecule	r_{AB} [16, 17] (Å)	$(e.I.\, r_{AB})_{calc.}$	$\mu_{AB_{exp.}}$ [a]
HF	0.92	1.81	1.91
HCl	1.27	1.74	1.03
HBr	1.41	1.27	0.78
HI	1.61	0.30	0.38
LiF	1.55	5.34	6.33 [19]
LiCl	2.02	6.45	5.9 [20] 7.12 [21]
LiBr	2.17	6.66	6.25
LiI	2.39	6.77	7.07
NaF	1.84	6.68	8.37 [22]
NaCl	2.36	8.18	8.50
NaBr	2.50	8.34	9.12 [19]
NaI	2.71	8.50	9.23 [19]
KF	2.13	8.51	8.62
KCl	2.67	10.36	10.27 [19]
KBr	2.82	10.68	10.41
KI	3.05	11.11	11.05 [23]
RbF	2.27	9.17	8.54 [19]
RbCl	2.79	11.00	10.60
RbBr	2.94	11.34	10.5
RbI	3.18	11.82	—
CsF	2.35	9.70	7.87
CsCl	2.91	11.65	10.50
CsBr	3.07	12.08	10.7
CsI	3.32	12.56	12.1 [23]

[a] Taken from Ref. [18], unless otherwise indicated.

other evaluation of the covalent bond energy term. A more detailed description of this term, especially its influence upon the heteropolar bond stability, will be given in a forthcoming paper.

3. Conclusion

It seems that it is very important to obtain the true value for the covalent bonding power (electronegativity) of an element, especially for halogens and hydrogen, since finally these values will determine the heteropolar bond strength and the different contributions to the latter, i.e. covalent and ionic energy terms. Unfortunately, this true value is not always constant and depends upon the nature of the bonding partner and a quantitative distinction between all the effects involved, of which lone electron pair repulsion is relatively the most important, is not yet possible.

However, the evaluation of a mean covalent bonding power by means of an *a priori* crude extrapolation method, already allows one to calculate bond energy values, which are almost as accurate as those obtained by Evans and Huheey [1], who used a much more complicated bond energy function. This is the result of the conclusions reached at earlier [3], regarding the contributions to the bond energy and the conditions for bond equilibrium.

Although this treatment tends to support the suppositions made by Pauling for the description of the heteropolar bond energy, the conflict between Pauling's rule and Pearsons' is for a great deal to be ascribed to:

1) the less correct formulation of the equations for covalent and ionic energy terms by Pauling;

2) the absence of more absolute electronegativity values in the latter; and

3) the neglect of the variation in covalent bonding power (electronegativity) of an element in going from one bond to another, the latter being important in the cases, given above.

Several attempts have already been made to calculate bond energies in polyatomic molecules as well [1, 2b] with reasonable succes, but the presence of polyvalent atoms in these molecules will introduce additional terms into the bond energy function now used, such as the hybridization state of the central element, rehybridization effects and non-bonding repulsion between substituents. A semiquantitative evaluation of some of these effects will soon be reported.

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