centrations too low to be detected by Raman spectroscopy cannot be excluded. Such an ionization could also contribute to the conductivity of these mixtures.

Acknowledgment. This work has been supported by the Hellenic General Secretariat of Research and Technology and the EEC "SCIENCE" program.

Registry No. Hg, 7439-97-6; $HgCl_2$, 7487-94-7; $HgBr_2$, 7789-47-1; HgI_2, 7774-29-0; HgF_2, 7783-39-3; $Hg_3(AlCl_4)_2$, 36554-82-2.

Contribution from the Heavy Water Division,
Bhabha Atomic Research Centre, Bombay 400085, India

Electronegativity, Hardness, and Chemical Binding in Simple Molecular Systems

Tapan K. Ghanty and Swapan K. Ghosh*

Received September 16, 1991

A new electronegativity-based approach to chemical binding is proposed where the covalent binding is formulated in terms of the accumulation of electron density at the bond center using the concepts of bond electronegativity and bond hardness. In an AB_n type molecule, the covalent contribution to the single A–B bond energy is shown to be given by a simple expression in terms of the A–A and B–B bond energies. For heteronuclear diatomic molecules, this reduces to an average of the geometric and arithmetic means of the bond energies of corresponding homonuclear diatomics. This covalent part together with the derived expression for the ionic contribution with no adjustable parameter constitutes the total bond energy expression. Predicted numerical results on bond energies and atomic charges of selected diatomic and simple polyatomic molecules are shown to agree well with available data.

Introduction

The concept of electronegativity, introduced originally by Pauling[1] and Mulliken,[2] has played a fundamental role in the conceptual development of all branches of chemistry.[3] The electronegativity defined as

$$\chi = -(\partial E/\partial N) \tag{1}$$

originally due to Pritchard and Sumner[4] as well as Iczkowski and Margrave[5] denotes the energy derivative with respect to number of electrons and is equal to $(I + A)/2$ in a finite difference approximation, where I and A represent ionization potential and electron affinity, respectively. This concept now rests on a profound theoretical basis within the framework of density functional theory[6] due to the work of Parr et al.,[7] who identified χ as the negative of the chemical potential μ of the electron cloud, viz.

$$\chi = -\mu = -(\delta E/\delta \rho) \tag{2}$$

where the functional derivative is with respect to the electron density $\rho(r)$. This definition provides not only a means of quantum mechanical calculation of χ but also a justification for the electronegativity equalization procedure used widely in chemistry.[3]

Another important quantity is the second derivative of energy identified[8] recently as a measure of chemical hardness[9]

$$\eta = \tfrac{1}{2}(\partial^2 E/\partial N^2) = \tfrac{1}{2}(\partial \mu/\partial N) \tag{3}$$

which equals $(I - A)/2$ in a finite difference approximation but can also be expressed in terms of electron density[10] and is thus amenable to a quantum mechanical calculation.

An understanding or prediction of molecule formation in terms of these atomic properties has been of much importance in chemistry. The electronegativity parameter governs the charge transfer in chemical binding and hence determines the polarity of the molecule. The binding energy of a molecule however consists of not only this charge-transfer contribution but also the energy involved in covalent bond formation—the latter being the only contribution for homonuclear molecules.

For a diatomic molecule AB, Pauling[1] has proposed that the covalent contribution can be approximated as the geometric mean of the corresponding homopolar bond energies, i.e.

$$D_{AB}^{cov} = (D_{AA}D_{BB})^{1/2} \tag{4}$$

and thus led to the bond energy equation[1]

$$D_{AB} = D_{AB}^{cov} + 30(\chi_A - \chi_B)^2 \tag{5}$$

where the last term denotes the energy (in kcal/mol) associated with the charge-transfer process.

Several other empirical equations have later been proposed; e.g., Matcha[11] has prescribed an equation of the form

$$D_{AB} = D_{AB}^{cov} + K\{1 - \exp[-(30/K)(\chi_A - \chi_B)^2]\} \tag{6}$$

with the empirical parameter K being equal to 103 for energy expressed in kcal/mol. Reddy et al.[12] have recently proposed a very simple formula of the form

$$D_{AB} = D_{AB}^{cov} + 32.058|\chi_A - \chi_B| \tag{7}$$

In eqs 4–7, D_{AB}^{cov} denotes the full covalent contribution to the bond energy. Sanderson[13] and Huheey,[14] however, have treated the

---

(1) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca NY, 1960.
(2) Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 782–793.
(3) Sen, K. D., Jorgensen, C. K., Eds. *Electronegativity: Structure and Bonding*; Springer-Verlag: Berlin, 1987; Vol. 66.
(4) Pritchard, H. O.; Sumner, F. H. *Proc. R. Soc. London* **1956**, *A235*, 136–143.
(5) Iczkowski, R. P.; Margrave, J. L. *J. Am. Chem. Soc.* **1961**, *83*, 3547–3551.
(6) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
(7) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801–3807.
(8) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 7512–7516.
(9) Pearson, R. G. *Hard and Soft Acids and Bases*; Dowden, Hutchinson, and Ross: Stroudsville, PA, 1973.
(10) Berkowitz, M.; Ghosh, S. K.; Parr, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 6811–6814. Ghosh, S. K. *Chem. Phys. Lett.* **1990**, *172*, 77–82.
(11) Matcha, R. L. *J. Am. Chem. Soc.* **1983**, *105*, 4859–4862.
(12) Reddy, R. R.; Rao, T. V. R.; Biswanath, R. *J. Am. Chem. Soc.* **1989**, *111*, 2914–2915.
(13) Sanderson, R. T. *Chemical Bonds and Bond Energy*; Academic: New York, 1976. Sanderson, R. T. *Polar Covalence*; Academic: New York, 1983.
(14) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper & Row: New York, 1983.

0020-1669/92/1331-1951$03.00/0

ionic and covalent contributions, D_{AB}^{ion} and D_{AB}^{cov}, respectively, as mutually exclusive and have thus expressed the bond energy as

$$D_{AB} = t_i D_{AB}^{ion} + (1 - t_i) D_{AB}^{cov} \tag{8}$$

consisting of partial ionic and covalent contributions with t_i as a measure of the partial ionic character.

Although electronegativity-based methods for the calculation of partial atomic charges in polar molecules have improved[15] considerably, the same for bond energy calculations are more empirical in status. Thus, the geometric mean expression for the covalent contribution is empirical; moreover, for simple polyatomic molecules of AB_n type, it is not even clear whether this quantity refers to the average covalent energy of the A–B bond in this molecule or the covalent contribution to the energy involved in the process $A + B \rightarrow AB$. It is also not known whether the full contribution D_{AB}^{cov} as in eqs 5–7 or the partial contribution $(1 - t_i)D_{AB}^{cov}$ as in eq 8 is to be used in a bond energy equation. The present work aims at clarifying these issues through "rigorous" derivations with well-defined procedures for simplification of the final bond energy equation.

In a purely covalent bond (e.g. for a homonuclear diatomic molecule), there is no net charge transfer between the atoms and hence procedures based on the concept of electronegativity, which is linked with charge transfer, are not directly applicable to the description of covalent binding. A bond formation is, however, accompanied by charge accumulation in the bond region which we exploit here to explain and formulate covalent binding within an electronegativity-based picture. Ghosh and Parr[16] have recently proposed the concept of bond electronegativity, by assigning an electronegativity value to the bond region to obtain a bond charge model and a semiempirical density functional theory. This is rigorous since the chemical potential is defined at each point in space and, therefore, an electronegativity value can be assigned to any region. A higher value of electronegativity at the bond region when two atoms (homo- or heteronuclear) are brought to the equilibrium distance would account for charge transfer to the bond region and hence covalent binding. The extent of this charge transfer is governed by the hardness of the bond region, which can also be defined rigorously,[16] using the concept of local hardness.[10,17]

In the present work, we derive an expression for the average bond energy of a simple AB_n type polyatomic molecule (and hence a heteronuclear diatomic molecule as a special case) as sum of covalent and ionic contributions. The covalent term is expressed in terms of the atomic electronegativity and hardness parameters and is also reformulated in terms of the bond energies of the corresponding homonuclear diatomics. The resulting expression for covalent contribution is related to but different from the geometric mean used earlier. Modifications of the ionic term can be introduced to obtain improved results. The expressions for the partial atomic charges and chemical potential (or electronegativity) of the molecule formed are also derived.

In what follows, we discuss the proposed bond electronegativity based model for chemical binding. The expressions for the bond energy and partial atomic charges are derived using suitable models for the bond electronegativity and the bond hardness parameters. Numerical results obtained from the present scheme are compared with available experimental or calculated results.

Bond Electronegativity Based Model for Chemical Binding

The formation of a chemical bond between two atoms A and B is considered here as a two-step process. In the first step due to electronegativity difference of the atoms, charge transfer takes place from A to B (assuming $\chi_B > \chi_A$) leading to the formation of two species $A^{*\delta+}$ and $B^{*\delta-}$ with their new electronegativities $\chi_A{}^*$ and $\chi_B{}^*$ getting equalized. In the second step, the two charged species are brought to equilibrium internuclear separation, when the chemical potential μ of the bond region becomes lower (note that $\mu = -\chi$) than those of the resulting atomic species, and hence further charge transfer takes place from the two charged atoms to the bond region to attain an equilibrium chemical potential which is same in the atomic as well as bond region. For the polyatomic AB_n molecule, the first step involves charge transfer between the atom A and n number of B atoms, while, in the second step, there is charge transfer to each bond region from the charged atom A and the corresponding charged atom B. While the energy associated with the first step corresponds to the ionic contribution to the bond energy, that for the second step corresponds to covalent bonding. In the case of binding in a homonuclear diatomic molecule, only the second process contributes. Thus, chemical binding is essentially viewed here as a charge-transfer and reorganization effect.

Energy of an atom A as a function of the number of electrons N_A is given by

$$E_A = E_A^0 + \mu_A^0 \Delta N_A + \eta_A^0 (\Delta N_A)^2 \tag{9}$$

where E_A^0 corresponds to the energy of the neutral atom with N_A^0 number of electrons, μ_A^0 and η_A^0 are the corresponding chemical potential and hardness, respectively, and $\Delta N_A = N_A - N_A^0$. The chemical potential μ_A corresponding to N_A electrons is

$$\mu_A = \mu_A^0 + 2\eta_A^0 \Delta N_A \tag{10}$$

Consider now the first step for an AB_n molecule, viz. the charge transfer from A to each of the n number of B atoms, determined by the equalization of chemical potential $\mu_A = \mu_B$. Using eq 10 with $\Delta N_A + n\Delta N_B = 0$, one has the results

$$\Delta N_A = {}^1\!/_2 (\mu_B^0 - \mu_A^0)/(\eta_A^0 + \eta_B^0/n) \tag{11}$$

$$\mu_A = \mu_B = \mu_A{}^* = \mu_B{}^* = \mu^* = (\eta_A^0 \mu_B^0 + \mu_A^0 \eta_B^0/n)/(\eta_A^0 + \eta_B^0/n) \tag{12}$$

and the energy involved in the charge-transfer process is

$$\Delta E^{ion} = -{}^1\!/_4 (\mu_A^0 - \mu_B^0)^2/(\eta_A^0 + \eta_B^0/n) \tag{13}$$

which can be considered as the ionic contribution to the total bond energy of the molecule AB_n.

Consider now the second step where each of the n charged species $B^{*\delta-}$ is placed at a distance R from $A^{*n\delta+}$, where R is the equilibrium A–B bond length of the molecule AB_n. Considering the chemical potential and hardness of each bond region to be $\mu_{bond}{}^*$ and $\eta_{bond}{}^*$, respectively, one has

$$\Delta E_A^{cov} = \mu_A{}^* \Delta N_A{}^* + \eta_A{}^* (\Delta N_A{}^*)^2 \tag{14a}$$

$$\Delta E_B^{cov} = \mu_B{}^* \Delta N_B{}^* + \eta_B{}^* (\Delta N_B{}^*)^2 \tag{14b}$$

$$\Delta E_{bond}^{cov} = \mu_{bond}{}^* \Delta N_{bond} + \eta_{bond}{}^* (\Delta N_{bond})^2 \tag{14c}$$

and

$$\mu_A = \mu_A{}^* + 2\eta_A{}^* \Delta N_A{}^* \tag{15a}$$

$$\mu_B = \mu_B{}^* + 2\eta_B{}^* \Delta N_B{}^* \tag{15b}$$

$$\mu_{bond} = \mu_{bond}{}^* + 2\eta_{bond}{}^* \Delta N_{bond} \tag{15c}$$

Equating the three equations (15a–c) and using the charge conservation

$$\Delta N_A{}^* + n\Delta N_B{}^* + n\Delta N_{bond} = 0$$

and also the result that $\mu_A{}^* = \mu_B{}^*$, one obtains

$$\Delta N_A{}^* = \{\eta_B{}^*(\mu_{bond}{}^* - \mu_A{}^*)\}/\{2[\eta_{bond}{}^*(\eta_A{}^* + \eta_B{}^*/n) + \eta_A{}^*\eta_B{}^*]\} \tag{16a}$$

$$\Delta N_B{}^* = \{\eta_A{}^*(\mu_{bond}{}^* - \mu_B{}^*)\}/\{2[n_{bond}{}^*(\eta_A{}^* + \eta_B{}^*/n) + \eta_A{}^*\eta_B{}^*]\} \tag{16b}$$

$$\mu_A = \mu_B = \mu_{bond} = \mu_{mol} = \{\mu_{bond}{}^*\eta_A{}^*\eta_B{}^* + \eta_{bond}{}^*(\eta_A{}^* + \eta_B{}^*/n)\mu_A{}^*\}/\{\eta_A{}^*\eta_B{}^* + \eta_{bond}{}^*(\eta_A{}^* + \eta_B{}^*/n)\} = \{\mu_{bond}{}^* + (1/n)(\eta_{bond}{}^*/\eta_{HM})\mu_A{}^*\}/\{1 + (1/n)(\eta_{bond}{}^*/\eta_{HM})\} \tag{17}$$

where

---

(15) Mortier, W. J.; Ghosh, S. K.; Shankar, S. *J. Am. Chem. Soc.* **1986**, *108*, 4315–4320 and references therein.

(16) Ghosh, S. K.; Parr, R. G. *Theoret. Chim. Acta* **1987**, *72*, 379–391.

(17) Ghosh, S. K.; Berkowitz, M. *J. Chem. Phys.* **1985**, *83*, 2976–2983.

$$\eta_{\mathrm{HM}} = \eta_{\mathrm{A}}^{*}(\eta_{\mathrm{B}}^{*}/n)/(\eta_{\mathrm{A}}^{*} + \eta_{\mathrm{B}}^{*}/n) \tag{18}$$

is the harmonic mean of η_A^* and η_B^*/n. The covalent energy is given by the sum

$$\Delta E^{\mathrm{cov}} = \Delta E_{\mathrm{A}}^{\mathrm{cov}} + n\Delta E_{\mathrm{B}}^{\mathrm{cov}} + n\Delta E_{\mathrm{bond}}^{\mathrm{cov}} = -(\mu^{*} - \mu_{\mathrm{bond}}^{*})^2/\{4(\eta_{\mathrm{bond}}^{*}/n + \eta_{\mathrm{HM}})\} \tag{19}$$

with $\mu^* = \mu_A^* = \mu_B^*$ after the first step charge transfer.

At this point we introduce models for the quantities μ_{bond}^* and η_{bond}^*. It is established[18] that the chemical potential of an atom is nearly equal to the electrostatic potential at the covalent radius. Since the electrostatic potential is additive, the chemical potential at the point of contact of the Wigner–Seitz spheres for two atoms can be modeled as the sum of the individual chemical potentials. Thus, μ_{bond}^* can be modeled as

$$\mu_{\mathrm{bond}}^{*} = (\mu_{\mathrm{A}}^{*} + \mu_{\mathrm{B}}^{*}) \tag{20a}$$

The parameter η_{bond}^* can also be assumed to be proportional to η_{HM}, the harmonic mean of individual hardnesses of all the atoms in AB_n molecule as defined in eq 18, i.e.

$$\eta_{\mathrm{bond}}^{*} = k_1\eta_{\mathrm{HM}} \tag{20b}$$

This modeling is motivated by the fact that the molecular hardness is proportional to the harmonic mean of atomic hardnesses.[19] It may be noted that somewhat different models for μ_{bond} and η_{bond} as explicit functions of the internuclear distance R were proposed in the work of Ghosh and Parr.[16] Their modeling for homonuclear diatomics led to a simple density functional version of the bond charge model of Parr and Borkman[20] as well as a semiempirical density functional theory which have been further discussed by Parr and Yang.[6] The objective here is to model these quantities solely in terms of the atomic chemical potential and hardness parameters. The connection between the two models can be established by introducing suitable R-dependent coefficients in eqs 20. With the two models for μ_{bond}^* and η_{bond}^* of eqs 20, the expression (19) for ΔE^{cov} becomes

$$\Delta E^{\mathrm{cov}} = -(\tfrac{1}{4}\eta_{\mathrm{HM}})(\mu^{*})^2/(1 + k_1/n) \tag{21}$$

Using eq 12, the covalent single bond energy $D_{\mathrm{AB}}^{\mathrm{cov}}$ $(=-\Delta E^{\mathrm{cov}}/n)$ can be expressed as

$$D_{\mathrm{AB}}^{\mathrm{cov}} = [\eta_{\mathrm{HM}}/4(n + k_1)]\{(\mu_{\mathrm{A}}^{0}/\eta_{\mathrm{A}}^{0}) + n(\mu_{\mathrm{B}}^{0}/\eta_{\mathrm{B}}^{0})\}^2 \tag{22}$$

For the covalent bond energies D_{AA} and D_{BB} of the homonuclear diatomics A_2 and B_2, respectively, eq 22 leads to the result

$$D_{\mathrm{AA}} = [\tfrac{1}{2}(1 + k_1)][(\mu_{\mathrm{A}}^{0})^2/\eta_{\mathrm{A}}^{0}] \tag{23}$$

and a similar expression for D_{BB}. Thus, the covalent bond energy of eq 22 can be expressed as

$$D_{\mathrm{AB}}^{\mathrm{cov}} = \{(1 + k_1)/(n + k_1)\}\{1/(n\eta_{\mathrm{A}}^{0} + \eta_{\mathrm{B}}^{0})\} \{\eta_{\mathrm{B}}^{0}D_{\mathrm{AA}}/2 + n^2\eta_{\mathrm{A}}^{0}D_{\mathrm{BB}}/2 + n(\eta_{\mathrm{A}}^{0}\eta_{\mathrm{B}}^{0})^{1/2}(D_{\mathrm{AA}}D_{\mathrm{BB}})^{1/2}\} \tag{24}$$

Apart from the homonuclear bond energies, this expression consists also of the relative hardnesses of the two atoms. One can further simplify this expression by assuming $\eta_A^0 \approx \eta_B^0$, which is reasonable since Pearson's[9] conjecture "hard likes hard" and "soft likes soft" works in most of the cases. This leads to the result

$$D_{\mathrm{AB}}^{\mathrm{cov}} = \{(1 + k_1)/(n + k_1)\}\{n/(n + 1)\} \times \{(D_{\mathrm{AA}}D_{\mathrm{BB}})^{1/2} + \tfrac{1}{2}(nD_{\mathrm{BB}} + D_{\mathrm{AA}}/n)\} \tag{25}$$

For a diatomic molecule AB, this expression simplifies to

$$D_{\mathrm{AB}}^{\mathrm{cov}} = \tfrac{1}{2}[(D_{\mathrm{AA}} + D_{\mathrm{BB}})/2 + (D_{\mathrm{AA}}D_{\mathrm{BB}})^{1/2}] \tag{26}$$

which indicates that the covalent contribution in a diatomic molecule is the average of the geometric mean D_{GM} and the arithmetic mean D_{AM} and is different from the geometric mean result proposed by Pauling.[1] It also establishes that this expression represents the net covalent contribution and should not be weighted by any factor like t_i in the total energy calculation as used in eq 8.

Table I. Atomic Electronegativity, Hardness Parameters, and Bond Energies of Homonuclear Diatomic Molecules

atoms (A)	electronegativity[a] (χ_A), eV	hardness[a] (η_A), eV	homonuclear bond energy,[b] (D_{AA}), kcal/mol
Na	2.8	2.335	17.30
K	2.9	1.440	11.80
Rb	2.09	2.090	10.80
Ca	3.30	2.370	25.00
Mg	4.09	3.010	31.00
Sr	3.14	2.205	20.00
As	5.345	4.015	35.00
Sb	4.965	3.785	29.00
C	5.805	5.465	82.60
F	12.18	8.680	37.00
Cl	9.38	5.650	57.30
Br	8.40	4.700	45.45
I	8.10	4.575	35.60

[a] The values of χ and η are calculated from ionization potential and electron affinity data from ref 21. [b] D_{AA} values are from ref 14.

The total single A–B bond energy in AB_n should therefore be represented as the sum of the ionic contribution given by eq 13 and the covalent contribution of eq 25, i.e.

$$D_{\mathrm{AB}} = D_{\mathrm{AB}}^{\mathrm{cov}} + (\tfrac{1}{4}n)(\mu_{\mathrm{A}}^{0} - \mu_{\mathrm{B}}^{0})^2/(\eta_{\mathrm{A}}^{0} + \eta_{\mathrm{B}}^{0}/n) \tag{27}$$

The partial atomic charges on atoms A and B can also be calculated easily. After the charge-transfer processes in steps 1 and 2, the net charge on the central atom A is $q_A = -(\Delta N_A + \Delta N_A^*)$, and a net negative charge equal to $(\Delta N_A^*/n + \Delta N_B^*)$ is accumulated at each of the n bond centers, where ΔN_A is given by eq 11 and ΔN_A^* and ΔN_B^* given by eqs 16 can be rewritten as

$$\Delta N_{\mathrm{A}}^{*} = \{n/(n + k_1)\}\mu_{\mathrm{A}}^{*}/2\eta_{\mathrm{A}}^{0} = \{n/(n + k_1)\}\{\tfrac{1}{2}\eta_{\mathrm{A}}^{0}\}(\eta_{\mathrm{A}}^{0}\mu_{\mathrm{B}}^{0} + \mu_{\mathrm{A}}^{0}\eta_{\mathrm{B}}^{0}/n)/(\eta_{\mathrm{A}}^{0} + \eta_{\mathrm{B}}^{0}/n) \tag{28a}$$

$$\Delta N_{\mathrm{B}}^{*} = \{n/(n + k_1)\}\mu_{\mathrm{B}}^{*}/2\eta_{\mathrm{B}}^{0} = \{n/(n + k_1)\}\{\tfrac{1}{2}\eta_{\mathrm{B}}^{0}\}(\eta_{\mathrm{A}}^{0}\mu_{\mathrm{B}}^{0} + \mu_{\mathrm{A}}^{0}\eta_{\mathrm{B}}^{0}/n)/(\eta_{\mathrm{A}}^{0} + \eta_{\mathrm{B}}^{0}/n) \tag{28b}$$

To obtain the net partial atomic charges, each bond charge $(\Delta N_A^*/n + \Delta N_B^*)$ has to be partitioned between the two atoms A and B. If f_A and f_B $(=(1 - f_A))$ are the fractions of this charge that is considered to belong to the respective atoms, then the net charge on atom A is given by

$$q_{\mathrm{A}} = -(\Delta N_{\mathrm{A}} + \Delta N_{\mathrm{A}}^{*}) + nf_{\mathrm{A}}(\Delta N_{\mathrm{A}}^{*}/n + \Delta N_{\mathrm{B}}^{*}) = \tfrac{1}{2}(\mu_{\mathrm{A}}^{0} - \mu_{\mathrm{B}}^{0})/(\eta_{\mathrm{A}}^{0} + \eta_{\mathrm{B}}^{0}) - (\tfrac{1}{2}\eta_{\mathrm{A}}^{0})\{n/(n + k_1)\}\{(\eta_{\mathrm{A}}^{0}\mu_{\mathrm{B}}^{0} + \mu_{\mathrm{A}}^{0}\eta_{\mathrm{B}}^{0}/n)/(\eta_{\mathrm{A}}^{0} + \eta_{\mathrm{B}}^{0}/n)\} + f_{\mathrm{A}}\{n/(n + k_1)\}[(\mu_{\mathrm{A}}^{0}/\eta_{\mathrm{A}}^{0}) + (\mu_{\mathrm{B}}^{0}/(\eta_{\mathrm{B}}^{0}/n))] \tag{29}$$

with an analogous expression for q_B which will clearly be equal to $-q_A/n$. Equations 27–29 provide expressions for the bond energy and the partial atomic charges in a simple polyatomic molecule AB_n.

Results and Discussion

The average bond energy and the partial atomic charges in AB_n type molecules can thus be calculated using eqs 27 and 29, respectively. Modeling the bond hardness via eqs 20b has however introduced a parameter k_1, which is assumed to have a value of 1.5 for calculations in the present work. The value $k_1 = 1$ is equivalent to assuming a harmonic mean for the bond hardness, while $k_1 = 2$ corresponds to assuming an arithmetic mean postulate[19] for the bond softness (reciprocal of hardness). For the partial atomic charges, the partitioning of the bond charge has been imposed using the fractional parameter f_A, which can be assumed to be equal to half or can be prescribed from the relative electronegativity values. Here we have chosen f_A to be equal to

---

(18) Politzer, P.; Parr, R. G.; Murphy, D. R. *Phys. Rev. B* **1985**, *31*, 6809–6810.

(19) Yang, W.; Lee, C.; Ghosh, S. K. *J. Phys. Chem.* **1985**, *89*, 5412–5414.

(20) Parr, R. G.; Borkman, R. F. *J. Chem. Phys.* **1968**, *49*, 1055–1058.

Table II. Bond Dissociation Energies (D_{AB}) and Partial Atomic Charges (q_A) of Selected Polytomic Molecules

molecule (AB_n)	D_{AB}^{exp} [a]	D_{AB}^{cal} [b]	q_{cal} [c]	q_{data} [d]
NaF	114.0	118.3	0.74	0.92
NaCl	97.5	96.9	0.69	0.79
NaBr	86.7	81.1	0.65	0.76
NaI	72.7	72.5	0.62	0.71
KF	117.0	120.8	0.91	0.84
KCl	101.0	98.6	0.87	0.80
KBr	90.5	82.7	0.83	0.78
KI	78.0	73.9	0.81	0.74
RbF	117.0	130.9	0.78	0.78
RbCl	106.0	108.6	0.76	0.78
RbBr	92.0	92.7	0.74	0.77
RbI	79.0	83.9	0.72	0.75
MgF_2	123.0	114.4	1.08	
$MgCl_2$	97.0	92.5	0.86	
$MgBr_2$	81.0	73.2	0.74	
MgI_2	63.0	62.7	0.70	
CaF_2	132.0	136.7	1.29	
$CaCl_2$	103.0	109.8	1.12	
$CaBr_2$	96.0	88.3	1.01	
CaI_2	78.0	76.9	0.97	
SrF_2	132.0	140.9	1.35	
$SrCl_2$	112.0	112.7	1.19	
$SrBr_2$	97.0	90.9	1.09	
SrI_2	80.0	79.4	1.04	
AsF_3	115.7	92.5	1.03	
$AsCl_3$	76.9	78.1	0.68	
$AsBr_3$	61.7	60.3	0.51	
AsI_3	47.8	49.9	0.46	
SbF_3	105.0	98.7	1.12	
$SbCl_3$	75.2	81.2	0.77	
$SbBr_3$	65.1	62.5	0.61	
SbI_3	46.6	51.9	0.55	
CF_4	116.0	89.1	0.85	
CCl_4	78.2	83.9	0.46	
CBr_4	68.0	66.4	0.28	
CI_4	51.0	55.1	0.24	

[a] Experimental bond dissociation energies are from ref 14. [b] Bond dissociation energies calculated using eqs 25 and 30. [c] Charges calculated using eq 29. [d] Charges calculated from dipole moment values from: Huber, K. B.; Herzberg, G. *Molecular Spectra and Molecular Structure, Constants for Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979; Vol. 4.

$\chi_A/(\chi_A + n\chi_B)$ for the purpose of calculation.

For the present calculations, the atomic electronegativity (χ_A) and hardness (η_A) parameters have been obtained from the ionization potential and electron affinity values and are shown in Table I along with the corresponding A–A bond energies which are used in bond energy equation. The bond energy eq 27 consists of contributions from the covalent as well as ionic terms. The covalent contribution is calculated using eq 25 and the single-bond energy data of Table I, while the ionic term is evaluated using the electronegativity and hardness parameters[21] of Table I and eq 27. The ionic contribution is however observed to be underestimated by the last term of eq 27, which might be a consequence of the neglect of electrostatic interaction between the charges. Inclusion of this interaction would change the denominator of the second term in eq 27 to $(\eta_A^0 + \eta_B^0/n - C/R)$, where $C = 14.14$ if η is expressed in electronvolts and the bond distance R is in angstroms. A detailed R-dependent theory can thus be developed, but we prefer to retain simplicity and express the ionic bond energy in terms of the atomic χ and η parameters alone. We therefore employ an approximate inverse dependence of η_A on the covalent radius R_A, given by $\eta_A \approx C/2R_A$ to eliminate the R-dependence. This, on assuming $R_A \approx R_B$, leads to the result $(\eta_A^0 + \eta_B^0/n) \approx (C/R)(1 + 1/n)$, using which we obtain $(\eta_A^0 + \eta_B^0/n - C/R) \approx [1 - \{1/(1 + n)\}](\eta_A^0 + \eta_B^0/n) = [1/(1 + n)](\eta_A^0 + \eta_B^0/n)$. Motivated by this approximate relation, we propose to introduce a multiplicative prefactor $1/(1 + n)$ in the denominator of the ionic term of eq 27 so as to obtain the modified bond energy equation

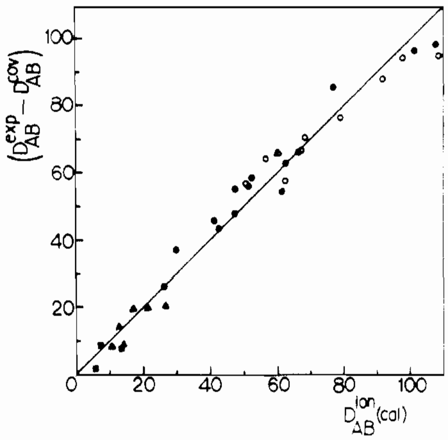

Figure 1. Plot of the ionic contribution to A–B bond energy ($D_{AB}^{exp} - D_{AB}^{cov}$) vs the calculated quantity D^{ion}(cal) given by the last term of eq 30 for selected AB_n molecules. The symbols ○, ●, ▲, and ⊡ correspond to the halides with n = 1–4, respectively.

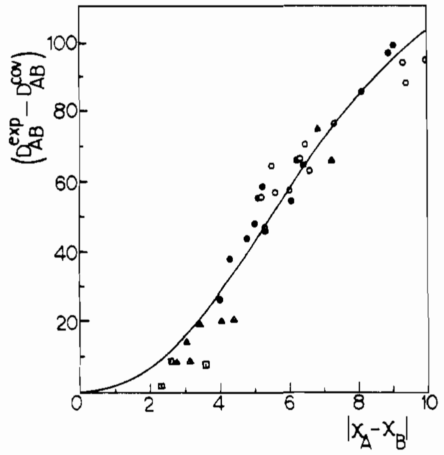

Figure 2. Plot of the ionic contribution to A–B bond energy ($D_{AB}^{exp} - D_{AB}^{cov}$) vs the electronegativity difference $|\chi_A - \chi_B|$ for selected AB_n molecules. The symbols ○, ●, ▲, and ⊡ correspond to the halide molecules with n = 1–4, respectively. The continuous curve corresponds to the last term of eq 31.

$$D_{AB} = D_{AB}^{cov} + \tfrac{1}{4}(1 + 1/n)(\chi_A^0 - \chi_B^0)^2/(\eta_A^0 + \eta_B^0/n) \qquad (30)$$

The last term is to be multiplied by a factor 23.06 for conversion to the units of kcal/mol, if χ and η are expressed in electronvolts.

The numerical results on bond energies calculated using eq 30 are compared with the experimental values in Table II. The overall agreement is quite good. The average percentage error is only 5.7, and this even reduces to 4.7 if one excludes the two fluoride compounds AsF_3 and CF_4. The adequacy of the expression is also reflected from the plot in Figure 1, where the quantity $D^{ion}(exp) = (D_{AB}^{exp} - D_{AB}^{cov})$ is plotted against D^{ion}(cal), given by the last term of eq 30, for a number of molecules contained in Table I. The numerical results on the partial atomic charges are also reported in Table II. For comparison, we have included the atomic charges obtained from available dipole moment values. An overall good agreement is observed in all cases.

While the present ionic term consists of two atomic parameters, viz. the electronegativity and hardness, alternative expression for the ionic contribution can be proposed in terms of the electronegativity difference $|\Delta\chi| = |\chi_A - \chi_B|$ alone in the spirit of the empirical equations proposed by Pauling,[1] Matcha,[11] or Reddy et al.,[12] as given by eqs 5–7. We suggest a two-parameter equation given by

$$D_{AB} = D_{AB}^{cov} + a(\Delta\chi)^2\{1 - \exp[-(b/\Delta\chi)^2]\} \qquad (31)$$

A comparison of the points in Figure 2 obtained by a plot of the

---

(21) Hinze, J.; Jaffe, H. H. *J. Am. Chem. Soc.* **1962**, *84*, 540–546. Hinze, J.; Jaffe, H. H. *J. Phys. Chem.* **1963**, *67*, 1501–1506. Hinze, J.; Whitehead, M. A.; Jaffe, H. H. *J. Am. Chem. Soc.* **1963**, *85*, 148–154.

quantity $D^{\rm ion}(\exp) = (D^{\rm exp}_{\rm AB} - D^{\rm cov}_{\rm AB})$ against $|\Delta\chi|$ and the continuous curve corresponding to the plot of $D^{\rm ion}(\rm cal)$, the last term of eq 31 against $|\Delta\chi|$, shows quite good agreement. The percentage error in the predicted bond energies based on eq 31 is only 6.8 for the parameters a and b equal to 1.768 and 9.381 when $\Delta\chi$ is expressed in electronvolts and the energy in kcal/mol. Equation 31 resembles that of Matcha[11] and gives similar behavior in the low- and high-value limits for $|\Delta\chi|$. The points in Figure 2 show that a proportionality to $|\Delta\chi|$ as given by Reddy et al.[12] (see eq 7) is not a good approximation, especially for polyatomic molecules.

The novel feature that has emerged in this work is a "rigorous" derivation of covalent binding energy within an electronegativity-based picture. While the derivation of the geometric mean–arithmetic mean results of eqs 25 and 26 have been mainly emphasized so far, the basic relations (22) and (23) directly give the covalent bond energy of the A–B bond in the AB_n molecule and the A–A bond energy, respectively, in terms of the χ and η parameters of the constituent atoms. An equation similar to eq 23 determining the bond energy of homonuclear diatomic molecules has recently been proposed[22] and is found to yield reasonably good results for the energy quantities. However, emphasis here has been on the calculation of the covalent contribution to heteronuclear bond energies from the corresponding homonuclear ones and also new formulation for the ionic contribution to the bond energy as given in eq 30.

Concluding Remarks

The present work is concerned with a description of chemical binding in simple polyatomic molecules (AB_n type) through the electronegativity and hardness parameters of the constituent atoms. The key novel feature has been the prediction of the covalent contribution to bond energy using the concepts of bond electronegativity and bond hardness. For a heteronuclear diatomic molecule, the covalent contribution is shown to be given by an average of the geometric and arithmatic means of the bond energies of the corresponding homonuclear diatomics, while, for the covalent contribution to the A–B bond energies in polyatomic AB_n molecules, an n-dependent weighted average of A–A and B–B bond energies is predicted. This term along with a newly derived ionic term yields reasonably good estimates of bond dissociation energies. The present model also provides suitable schemes for obtaining the partial atomic charges. Further studies incorporating explicitly the effects of interaction between the charges as well as an extension to more complicated polyatomic molecules are in progress.

Acknowledgment. It is a pleasure to thank H. K. Sadhukhan for his kind interest and encouragement.

---

[22] Ghanty, T. K.; Ghosh, S. K. *J. Phys. Chem.* **1991**, *95*, 6512–6514.

Contribution from the Biomedicine and Health Program, Australian Nuclear Science and Technology Organisation,
Lucas Heights Research Laboratories, Private Mailbag No. 1, Menai, NSW 2234, Australia,
and College of Pharmacy, The Ohio State University, Columbus, Ohio 43210

Development of Carborane Synthons: Synthesis and Chemistry of (Aminoalkyl)carboranes

J. Gerald Wilson,*,† A. K. M. Anisuzzaman,‡ F. Alam,§ and A. H. Soloway*,‡

Received October 30, 1991

A number of (aminoalkyl)-1,2-*closo*-dodecaboranes have been synthesized to provide carboranes with a functional group for covalent incorporation into structures of potential use in the treatment of cancer by boron neutron capture therapy (BNCT). (Phthalimidoalkyl)acetylenes reacted with decaborane to give the corresponding carboranes; removal of the phthalimido group under mild conditions using sodium borohydride in 2-propanol furnished the (aminoalkyl)carboranes which were isolated as their hydrochloride salts. An alternative approach involved the conversion of an (iodoalkyl)- or a ((tosyloxy)alkyl)carborane to the azido derivative which gave the amine on hydrogenation. An effective way of attaching a carborane moiety to thiouracil, which is selectively taken up in melanoma cells, is illustrated by the acylation of two of these amines with thiouracil-5-carboxylic acid.

Introduction

The development of carborane synthons with functional groups capable of covalent incorporation into a variety of different structures offers the potential for synthesizing boron compounds for use in the treatment of cancer by boron neutron capture therapy[1] (BNCT). Use of the amino function and its derivatives has already been described involving various boron cluster compounds,[2–5] but in the case of the highly lipophilic carboranes, only the less basic arylamines have been described. The synthesis of related (aminoalkyl)carboranes has been one of our objectives, but their formation has been greatly complicated by the fact that strongly basic amines do degrade the carborane cluster, converting the closo structure to its anionic nido counterpart.[6–8]

The first example of an aminoalkylcarborane was the reported synthesis of 1-((*N*,*N*-diethylamino)methyl) carborane by the reaction of equimolar amounts of (*N*,*N*-diethylamino)-2-propyne and decaborane in refluxing benzene.[9] However, the reported yield was only 4% and does raise questions regarding its structure. Preparation of bis(aminomethyl)carborane was described by the reaction of bis(halomethyl)carborane with aqueous ammonia, but the product from this reaction was shown conclusively to be the *nido*-carborane derivative.[10] More recently, (aminomethyl)carborane was reported[11] to be formed by the action of hydrazine

---

[†] Australian Nuclear Science and Technology Organisation.

[‡] The Ohio State University.

[§] Present address: US Borax Research Corp., Anaheim, CA 92801.

(1) Barth, R. F.; Soloway, A. H.; Fairchild, R. G. *Cancer Res.* **1990**, *50*, 1061.
(2) Soloway, A. H.; Butler, D. N. *J. Med. Chem.* **1966**, *9*, 411.
(3) Davis, M. A.; Soloway, A. H. *J. Med. Chem.* **1967**, *10*, 730.
(4) Mizusawa, E. A.; Thompson, M. R.; Hawthorne, M. F. *Inorg. Chem.* **1985**, *24*, 1911.
(5) Sneath, R. L., Jr.; Wright, J. E.; Soloway, A. H.; O'Keefe, S. M.; Dey, A. S.; Smolnycki, W. D. *J. Med. Chem.* **1976**, *19*, 1290.
(6) Zakharkin, L. I.; Kalnin, V. N. *Tetrahedron Lett.* **1965**, *7*, 407.
(7) Hawthorne, M. F.; Wegner, P. A.; Stafford, R. C. *Inorg. Chem.* **1965**, *4*, 1675.
(8) Varadarajan, A.; Sharkey, R. M.; Goldgenberg, D. M.; Hawthorne, M. F. *Bioconjug. Chem.* **1991**, *2*, 102.
(9) Heying, T. L.; Ager, J. W.; Clark, S. L.; Mangold, D. J.; Goldstein, H. L.; Hillman, M.; Polak, R. J.; Szmanski, J. W. *Inorg. Chem.* **1963**, *2*, 1089.
(10) Zakharkin, L. I.; Grebennikov, A. V. *Izv. Akad. Nauk SSSR, Ser. Chim.* **1966**, 2019.
(11) Nakagawa, T.; Watanabe, H.; Yoshizaki, T. Japan Patent 7,031,940; *Chem. Abstr.* **1970**, *74*, 100213t.

0020-1669/92/1331-1955$03.00/0