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LETTERS

Influence of Electronegativity on Reactions Involving Triangular Three-Center, Two-Electron Bonds: The −2h*β* Effect

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The HMO method, which describes the variation of bond energies of two-center, two-electron bonds AB with an electronegativity difference $\Delta\chi$ by a hyperbolic relationship, is investigated and suggests that the bond energies of triangular three-center, two-electron bonds of the type AB_2 are described by a similar hyperbolic relationship that is displaced along the $\Delta\chi$ axis by the resonance integral β_{BB}. The mutual relationship of these idealized bond-energy/electronegativity difference curves provides a basis for rationalizing the observed influence of electronegativity on reactions involving three-center bonds in the gas and liquid phases. Using this analysis, the contribution of the B−B interaction to the strength of a three-center bond AB_2 can be dissected into two discrete components. These are (i) the extra "aromatic" energy due to cyclic conjugation of two electrons and (ii) a contribution that is determined by the electronegativity difference $\Delta\chi$ (proportional to the difference in the Coulomb integrals, i.e., $\alpha_A - \alpha_B = h$) and by the resonance integral β_{BB} for the B−B interaction. We refer to the second contribution, which can be positive or negative depending upon the value of h, as the $-2h\beta$ effect, as it is this term that characterizes the second contribution in the bond-energy equations.

Introduction

Pauling described an empirical relationship between two-center, two-electron [2*c*-2*e*] bond energies (*BE*) and electronegativity (χ) (eq 1).[1]

$$BE_{AB} = {}^1/_2[BE_{AA} + BE_{BB}] + 23[\chi_A - \chi_B]^2 \qquad (1)$$

The extra "ionic energy" of the bond A−B is related to the electronegativity difference $[\chi_A{-}\chi_B]$ but not to its direction because $[\chi_A{-}\chi_B]^2$ is always positive. In this article, we develop a semiquantitative model demonstrating that this is not the case for triangular three-center, two-electron [3*c*-2*e*] bonds,[3] which have a directional dependence on the electronegativity difference. This arises from an additional $-[\chi_A{-}\chi_B]$ term in the bond-energy equation resulting in the variation of bond energy being asymmetric with respect to that of [2*c*-2*e*] bonds (Figure 1). This conclusion is consistent with the influence of electronegativity on reactions involving interconversion of [2*c*-2*e*] and [3*c*-2*e*] bonds in both gas and liquid phases.

Using an HMO treatment,[2] where α_A and α_B are the Coulomb integrals and β_{AB} is the resonance integral, the covalent bond energy (BE_{AB}) of bond A−B relative to that of the atoms is given by eq 2. This equation has the form of a hyperbola with the minimum value of BE_{AB} occurring when $(\alpha_A - \alpha_B)$ is zero.

$$BE_{AB} = [(\alpha_A - \alpha_B)^2 + 4\beta_{AB}{}^2]^{1/2} \qquad (2)$$

$$BE_{AB} \approx {}^1/_2[BE_{AA} + BE_{BB}] + \frac{[\alpha_A - \alpha_B]^2}{[BE_{AA} + BE_{BB}]} \qquad (3)$$

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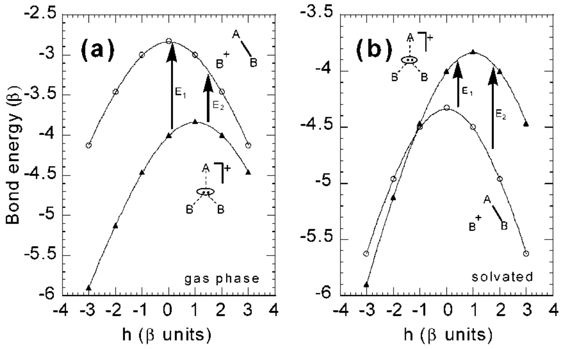
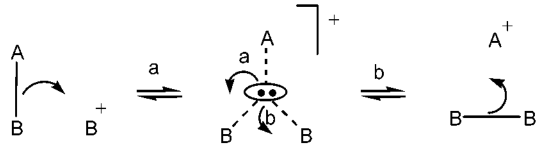


Figure 1. Variation of HMO bond energies with h for the systems **1** (○) and **2** (▲) in (a) the gas phase and (b) solution.

Dewar showed that eq 2 can be approximated to the form of eq 3.[4] Because Coulomb integrals are related to electronegativities [$\alpha_A - \alpha_B = K(\chi_A - \chi_B)$],[2] eq 3 may, under limited conditions, provide a theoretical basis for Pauling's empirical relationship (eq 1) and rationalizes the use of a $[\chi_A - \chi_B]^2$ term rather than an energetically more realistic $|\chi_A - \chi_B|$ term.[5] The general validity of Pauling's equation is now questionable.[5] Nevertheless, when applied to closely related series of molecules, these simple approaches do provide a model of heteroatomic covalent [2*c*-2*e*] bonds consistent with experimental observation, and we were encouraged to extend the approach to a semiquantitative model of [3*c*-2*e*] bonds.

Three-Center Bond Energies



1 **2** **3**

Consider the [3*c*-2*e*] bond **2**. Let the Coulomb integrals of the atoms A and B be α_A and α_B. Using the usual convention,[2] the difference between the values of these integrals is denoted by h (i.e., $\alpha_A - \alpha_B = h$). The value of h is therefore directly related to the electronegativity difference [$h = K(\chi_A - \chi_B)$ or $h \propto \Delta\chi$]. If the resonance integrals are β_{AB} and β_{BB}, the HMO secular determinant for bond **2** is

$$\begin{vmatrix} \alpha_B + h - E & \beta_{AB} & \beta_{AB} \\ \beta_{AB} & \alpha_B - E & \beta_{BB} \\ \beta_{AB} & \beta_{BB} & \alpha_B - E \end{vmatrix} = 0$$

Expanding gives

$$-E^3 + (3\alpha_B + h)E^2 - [3\alpha_B^{\,2} + 2\alpha_B h - (\beta_{BB}^{\,2} + 2\beta_{AB}^{\,2})]E + \alpha_B^{\,3} + h\alpha_B^{\,2} - h\beta_{BB}^{\,2} - \alpha_B(\beta_{BB}^{\,2} + 2\beta_{AB}^{\,2}) + 2\beta_{AB}^{\,2}\beta_{BB} = 0$$

and factorization gives eq 4,

$$[(\alpha_B - \beta_{BB}) - E][E^2 - (2\alpha_B + \beta_{BB} + h)E + (\alpha_B^{\,2} + h\alpha_B + h\beta_{BB} + \alpha_B\beta_{BB} - 2\beta_{AB}^{\,2})] = 0 \quad (4)$$

which has solutions

$$E = \alpha_B + {}^1/_2(\beta_{BB} + h) \pm {}^1/_2[h^2 - 2h\beta_{BB} + \beta_{BB}^{\,2} + 8\beta_{AB}^{\,2}]^{1/2} \quad \text{or} \quad E = \alpha_B - \beta_{BB}$$

The bond energy (BE_2) of bond **2** relative to that of $A^\bullet + B^\bullet + B^+$ (a convenient reference point) is therefore given by eq 5.

$$BE_2 = 2\alpha_B + h - 2E = -\beta_{BB} - [h^2 - 2h\beta_{BB} + \beta_{BB}^{\,2} + 8\beta_{AB}^{\,2}]^{1/2} \quad (5)$$

Here we assume that the Coulomb integral in the cation **2** (α_B) and the neutral species $B^\bullet$ and AB (α_B') are the same. In fact, they will differ ($\alpha_B' = \alpha_B + k$), but this difference will influence the bond energies only by a constant value, as will the change in core repulsion energy, which is also assumed to be constant. Like eq 2, eq 5 also has the form of a hyperbola, but it is displaced along the *x*-axis with BE_2 at a minimum when $h = \beta_{BB}$ (cf. Figure 1a).

Using the same approximations, the bond energy (BE_1) of the isoelectronic system **1** relative to that of $A^\bullet + B^\bullet + B^+$ is given by eq 6.[4]

$$BE_1 = -[h^2 + 4\beta'^{\,2}_{AB}]^{1/2} = -[h^2 + 8\beta_{AB}^{\,2}]^{1/2} \quad (6)$$

Note that the resonance integral β'_{AB} for bond A−B is not β_{AB} because (i) the bond lengths and overlap differ and (ii) AB is neutral. An estimate of β'_{AB} relative to β_{AB} can be obtained using second-moment scaling,[6] which gives $\beta'_{AB} = \sqrt{3}\beta_{AB}$. However, this estimation does not allow for the charge, which will increase the relative value of β_{AB}. For this analysis, we therefore prefer the relationship $\beta'_{AB} = \sqrt{2}\beta_{AB}$, which is incorporated into eq 6. This choice of proportionality constant is not critical because variation moves the curves only along the *y*-axis and does not affect the relative positions of the bond-energy curve minima on the *x*-axis, which depend only on β_{BB}.

Equations 5 and 6 show interesting similarities and differences. An important difference is that the bond energy of the [3*c*-2*e*] bond **2** contains an additional term $-2h\beta_{BB}$. We interpret the significance of the $-2h\beta_{BB}$ term when h is positive as representing the electronegative atom A removing electron density from the favorable bonding interaction between the other pair of atoms (BB) and thus reducing the bond energy. When h is negative, the reverse occurs. This effect is in addition to the favorable contribution of the electronegativity difference to the bond energy (h^2 term) that is common to both [3*c*-2*e*] and [2*c*-2*e*] bonds. The $-2h\beta_{BB}$ effect, which evolves naturally from the secular determinant, is, therefore, in satisfying agreement with chemical intuition.

Figure 1a shows a plot of eqs 5 and 6 (assuming $\beta_{AB} = \beta_{BB}$) against h. Note that the nonclassical system is the more stable in the gas phase. The "asymmetry" of the [3*c*-2*e*] bond curve, arising from the $-2h\beta_{BB}$ term, results in a significant variation in the energy separation of the two systems (i.e., $E_1 > E_2$) as the electronegativity difference measured by h varies. The absolute energy separation of the curves will depend on the choice of parameters α_B' and β'; these parameters effectively move the [2*c*-2*e*] bond hyperbola along the *y*-axis relative to the position of the [3*c*-2*e*] hyperbola but do not significantly change the shape of either curve.

Before examining specific examples of systems of the type AB_2, it is appropriate to consider the application of this model to a simple system of the type A_3. The best known example of a [3*c*-2*e*] bonded species in the gas phase is the ion H_3^+, which has equilateral triangular geometry. On the basis of eqs 5 and 6, the bond energies of [H_3^+] and [$H_2 + H^+$] are -4β and $-2\sqrt{2}\beta$, respectively, where β is the resonance integral in H_3^+. The bond lengths in these species are H_3^+ (0.9 Å) and H_2 (0.7 Å), and the semiquantitative assumption that $\beta_{H2} = \sqrt{2}\beta$ is not therefore unreasonable. The greater bond energy for the triangular species H_3^+ is consistent with the reaction $H_2 + H^+ \rightarrow H_3^+$ being exothermic in the gas phase. The core−core repulsion energy will also be greater in the triangular species, but this repulsion is clearly not sufficient to negate the extra bond energy derived from cyclic conjugation. In this example (H_3^+), the electronegativity difference ($\Delta\chi$ or h) between the atoms is zero, and there is no contribution to the bond energy from either h^2 or $-2h\beta$. In the next section, we explore how the variation of h influences the thermodynamics of reactions involving [3*c*-2*e*] bonds.

Reactions Involving Three-Center Bonds. Simple examples of gas-phase reactions involving [3*c*-2*e*] bonds are the protonation of C−H bonds of alkanes. For simple alkanes, the measured proton affinities (PA) (kcal mol^{-1}) are tBu-H 167, iPr−H ≤ 153, Et-H 132, and Me-H 127.[7] Because the electronegativity of the alkyl carbon increases along the series (i.e., h increases) this variation is in satisfactory agreement with Figure 1a (A = alkyl and B = H). The variation of calculated PAs of alkanonium dications[8] is also in agreement with this model.

In the liquid phase, solvation[9] will significantly affect the relative energies of the bond-energy curves. Because positive charge is concentrated on ion B^+ in **1** and spread over three atoms in **2**, the solvation energy will be greater for the classical system **1**. The solvent effect can be accommodated using a semiempirical constant in the bond-energy expression, and we have used a value of -1.5β to describe relative solvation. Figure 1b shows the bond-energy curves with this solvation parameter included in eq 6. For $h > -1$, species **2** now corresponds to a transition state or intermediate.

Figure 1b suggests that activation energies of such reactions will be related to the electronegativity difference (i.e., $E_1 < E_2$). This analysis is in good agreement with experimental observation. Olah et al.[10] have shown that isobutane in superacidic media at −78 °C undergoes only methine hydrogen exchange ($Me_3C{-}H \rightarrow Me_3C{-}D$); a higher temperature (0 °C) is necessary for exchange of the protons of the more electronegative methyl groups.[11] In general, the empirical reactivity order of alkane CH bonds is tertiary > secondary > primary.[12] Similarly, migratory aptitudes of substituents in carbocation 1,2 rearrangements increase as their electronegativity decreases (i.e., tBu > Et > Me),[13] and neglecting steric effects, both hydride and methide *sec-sec* 1,2 shifts can be expected to be faster than *tert-tert* 1,2 shifts.[14]

When the analysis is extended to formation of the bond **2** from a homonuclear [2*c*-2*e*] bond (i.e., **3** → **2**), an additional h term appears in the bond-energy equation. The bond energy (BE_3) of the system **3** relative to that of ($A^\bullet + B^\bullet + B^+$) is given by eq 7.

$$BE_\mathbf{3} = 2\alpha_B + h - 2(\alpha_B + \sqrt{2}\beta_{BB}) = h - 2\sqrt{2}\beta_{BB} \quad (7)$$

Note that choosing a different reference point (e.g., $A^+ + 2B^\bullet$) by definition gives different bond energies, but the energy differences between species **1**−**3** remain unchanged. Because only the relative energies are relevant, the conclusions are independent of the reference frame. The additional term h in eq 7 is therefore a real effect and arises from transfer of electron density from B to A. This situation does not arise in the heteronuclear case where electron density is already associated with A. Figure 2a shows a plot of the relative bond energies of species **2** and **3** in the gas phase. The variation of the energy difference with h significantly differs from that of the heteronuclear system (Figure 1a); the trend is reversed, with the energy difference increasing with h.

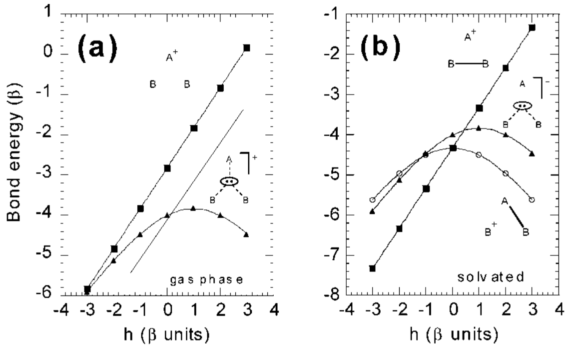


Figure 2. Variation of HMO bond energies with h for the systems **2** (▲) and **3** (■) in (a) the gas phase and (b) solution.

A simple reaction of the type **3** → **2** is the gas-phase hydrogenation of alkyl cations ($R_3C^+ + H_2 \rightarrow R_3CH_2^+$). Heats of hydrogenation for simple carbenium ions are ΔH (kcal mol^{-1}) Me_3C^+ −1, Me_2CH^+ ≤ −2.5, $MeCH_2^+$ −4, and CH_3^+ −40.[7] As the alkyl cation becomes more electronegative, the heat of hydrogenation increases in agreement with Figure 2a. Here it is important to distinguish between the carbonium ion and a van der Waals complex between the carbenium ion and hydrogen. More recent studies suggest that the hydrogenation of isopropyl and *tert*-butyl cations may be weakly endothermic and that the experimental values relate to van der Waals complexes.[15] If this is the case, then the true relationship is more realistically represented by the parallel line of lower energy in Figure 2a. The model has not been parametrized to fit experimental data, and variation of the parameters α' and β' together with allowance for core repulsion will move the bond-energy relationships up or down the *y*-axis. Taking this into account, the semiquantitative agreement with the available data is good. It can be appreciated why there is a rapid increase of ΔH with h and why the influence of h is the opposite of that for PAs. This model of homolytic [3*c*-2*e*] bond formation can be extended to the liquid phase (Figure 2b), in semiquantitative agreement with cationic reactions and Markovnikov's rule.

Conclusions

We believe that the semiquantitative HMO model developed above for small changes in electronegativity in similar systems describes a real effect when a pair of bonding electrons moves from a two-center to a cyclic three-center environment. The involvement of the term $-2h\beta$ at the HMO level, leading to "asymmetry" of the bond-energy curves, appears to account, at least in part, for a wide range of properties. The limitations of the HMO method are well-known, but historically it has provided sound insight into chemical bonding.[2] An advantage of the HMO method is access to analytical expressions from which cautious generalizations can be made; more sophisticated calculations are molecule-specific. We have not attempted to parametrize the model to reproduce energy differences. The value of this model is its use in rationalizing the mutual relationships of the bond-energy/electronegativity curves; to attempt to reproduce actual energies would push the model beyond its limitations.[2,16]

In organic chemistry, the influence of electronegativity on substituent effects (e.g., tBu vs Me) in cationic rearrangements is well-known. The effect is usually rationalized in terms of the less electronegative group (e.g., tBu) being better able to stabilize developing positive charge.[17] This and other factors, including steric and conformational effects, undoubtedly contribute. However, we now suggest that another contribution to this effect is the less electronegative substituent attracting less electron density away from the favorable bonding interaction between the other atom pair (i.e., $-2h\beta$ minimized). The influence of the $\chi_A - \chi_B$ variation will result in weakening of A$\cdots$B bonding in both **1** and **2** but strengthening of B$\cdots$B bonding in **2**, or vice versa. This predicted inverse variation of bonding is in good agreement with calculated C$\cdots$H and H$\cdots$H interatomic distances in protonated isobutane, propane,[15] and alkanonium dications.[8]

It is important to recognize that the electronegativity χ_R or Coulomb integral α_R of an alkyl radical R is directly related to hyperconjugation. The Coulomb integral of a tBu radical (IP 7.2 eV) is smaller than that of a Me radical (IP 9.8 eV) as a result of a hyperconjugative interaction between the singly occupied AO of the central carbon atom and the group orbitals of the substituents. This effect of hyperconjugation is reflected in the strengths of the corresponding [2*c*-2*e*] and [3*c*-2*e*] bonds by the values of α_R used in eqs 5 and 6. For the bonding of alkyl carbon atoms, the influence of electronegativity is not, therefore, an additional effect but is an alternative way of expressing the primary effect of hyperconjugation. Because bond energies are most easily expressed as functions of the Coulomb integral difference (h) and semiquantitative values for χ or α are reasonably accessible, a semiquantitative model using electronegativity rather than hyperconjugation is more accessible. Furthermore, because hyperconjugation is irrelevant for many three-center bonding systems (e.g., XH_2^+; X = H, Li, HBe)[18] and electronegativity difference is easier to express than hyperconjugation difference, a model based on electronegativity has more universal appeal than one that utilizes both concepts. Nevertheless, we emphasize the role of hyperconjugation in contributing to the $-2h\beta$ effect.

In conclusion, we have shown that a simple semiquantitative model of [3*c*-2*e*] bonds provides some insight into the structure and chemistry of these species. In addition to the examples discussed above, the model is consistent with linear [3*c*-2*e*] bonding becoming favored when h is large and β_{BB} is small (e.g., $[Li-H-Li]^+$ and $[Li-CH_3-Li]^+$),[19] especially when changes in nuclear repulsion and β_{AB} are considered. In particular, the adverse $-2h\beta$ effect, combined with low "aromaticity" (i.e., $-\beta_{BB}$ is small), may well contribute to reversing the relative stability of the linear and triangular isomers when $h \gg 0$, whereas triangular structures will always be favored when $h \leq 0$.

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