A SIMPLE THEORETICAL APPROACH TO BOND ENERGIES

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Abstract—The linear combination of fragment configurations (LCFC) method is used to study factors which control the relative strengths of bonds. Trends in bond strengths and the relative stability of structural isomers are predicted for a variety of organic molecules. It is argued that complex interactions within large organic molecules can be simplified to the interaction of the two electrons of a single bond. A compilation of experimental data is presented to support the proposed theoretical model.

The concept of the bond is a building block of chemistry. An understanding of the factors which determine the relative strength of covalent bonds is crucial for attacking problems of chemical structure and reactivity. Pauling,[2] Slater,[3] and Mulliken[4] proposed the criterion of maximum AO (atomic orbital) overlap for rationalizing relative bond strengths. Pauling also pointed out that "the energy of an actual bond between two unlike atoms is greater than the energy of a normal covalent bond between these atoms. This additional bond energy is due to the additional ionic character of the bond."[2a] This means that ionicity makes a bond stronger than it would have been, had it been purely covalent. Yet, there are trends in bond strengths which are not fully understood. For example, why is a Si–C bond weaker than a C–C bond, whereas, a Si–O bond is much stronger than a C–O bond? How does this question relate to the relative stability of disubstituted ethanes (such as 1 and 2) or to the relative stability of monosubstituted isomers of propane?

Specific answers to these questions would be capable of refining our understanding of the concept of a bond in polyatomic molecules.

In the past we have used the LCFC method[5,6] in which one estimates a bond strength, such as that of the central C–C bond in disubstituted ethanes 1 and 2, from the interaction of electronic configurations of the fragments which comprise the central bond. It was proposed that the central C–C bond in 1,1 homo-disubstituted ethanes (2) is stronger than the corresponding bond in the 1,2 homo-disubstituted isomers (1) because: (1) The MO overlap between the molecular fragments which comprise the two isomers is greater in the former. (2) The 1,1 isomer is comprised of a donor-acceptor pair of fragments, i.e. the central C–C bond has ionic character. This is not so in the case of the 1,2 isomer where as donor–donor (or acceptor–acceptor) fragment relationship exists. In fact the 1,1 homo-disubstituted isomers are generally found to be more stable than the corresponding 1,2 isomers.[6] Let us refine this treatment further.

1

Donor   Donor

2

Donor   Acceptor
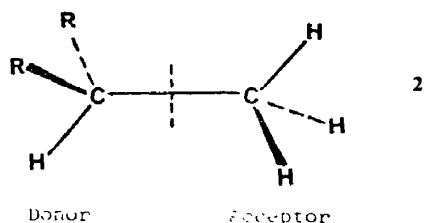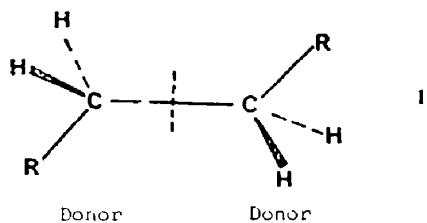
THEORY

Imagine an R–X bond as being made up by the union of the fragments R and X. The bond strength can be estimated from interaction of the electronic configurations, DA, D^+A^- and D^-A^+, which are generated by permuting the two electrons of the radical fragments, R· and X·, among their two frontier orbitals, ϕ_R and ϕ_X.[7] These configurations are shown below.

DA D^+A^- D^-A^+

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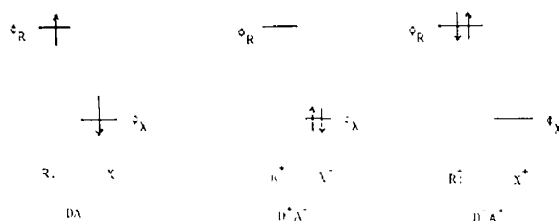
The fragments have naturally more orbitals than just ϕ_R and ϕ_X and one can use more configurations to describe the R $\Leftrightarrow$ X union. These configurations are of a local excited type, such as D*A, of a higher charge transfer type such as $D^{+2}A^{-2}$, or combination of charge transfer and local excitation (e.g. $D^{+}*A^{-}$). Some of these configuration (e.g. $D^{+2}A^{-2}$) are too high in energy to mix effectively, while others which can be quite low (e.g., D*A, D*A*), mix with the principle configurations in a way which does not contribute appreciably to the bond strength.[8] Our experience with the LCFC method shows that *on a qualitative level*, these configurations can be neglected without altering the trends set by the three principle configurations. Only when one looks at more subtle effects, such as the preferred conformation about the bond, should one include these other configurations (e.g. D*A*). In MO language their effects amount to non-bonded interactions such as the ones discussed in Part IV of Ref. 6b.[8]

The relative energies of the three configurations at infinite R X separation, are given by eqns (1) and (2) in terms of the ionization potential, I and the electron affinity, A.

$$E(D^-A\ ) - E(DA) = I_R - A_X \ (r = \infty) \qquad (1)$$

$$E(D\ A^+) - E(DA) = I_X - A_R \ (r = \infty). \qquad (2)$$

The energies of the ground state of R X, $= \psi_0$ and the two excited states ψ_1 and ψ_2, are determined by expanding the secular determinant obtained by neglecting the interfragmental overlap.[5e,f]

$$\begin{vmatrix} E(DA) - E & h & h \\ h & E(D^+A^-) - E & 0 \\ h & 0 & E(D^-A^+) - E \end{vmatrix} = 0 \qquad (3)$$

h is the interaction matrix element of DA with either D^+A^- or $D\ A^+$ and is negative. Within the approximation used, h equals $\sqrt{2}\beta_{RX}$, where β_{RX} is the resonance integral between the two singly occupied MOs in DA, $<\phi_R|\hat{H}|\phi_X>$.[9]

For purposes of understanding the qualitative trends, it is worthwhile having a quantitative scale of h, which varies with the nature of R and X, much the same as was done in setting the energy gaps in eqns (1) and (2). One can empirically approximate h using a Wolfsberg–Helmholtz type approximation,[10] in which the resonance integral is set proportional to the overlap integral S_{RX} and to the average of the ionization potentials of R and X. This means that h becomes more negative

$$h = K\left[\frac{I_R + I_X}{2}\right] S_{RX} \quad K < 0 \qquad (4)$$

as I_R and I_X increase, i.e. more electronegative groups will have larger .h.

The R X bond energy, E_b, is equal to the energy difference between ψ_0 at some equilibrium distance r_0, and DA at infinite distance (∞), adding to that the nuclear nuclear repulsion V_{nn} at r_0. Thus, E_b reads

$$E_b = E(\psi_0) - E(DA)\ - V_{nn}(r_0). \qquad (5)$$

This quantity can be obtained numerically from the exact solution of the 3×3 determinant. However, since one is interested in establishing *qualitative trends*,

one is better off deriving some approximate analytical forms for E_b. For this purpose one should take the entire bond-polarity spectrum (defined by the index $I_R - A_X$) starting from a homopolar bond for which at r_0 D^+A^- and D^-A^+ have approximately equal energy, both lying above DA and ending with a very polar bond in which D^+A^- lies below DA. This spectrum can be subdivided into three regions which are illustrated in Fig. 1.

(a) A nonpolar bond for which $E(D^+A^-) \approx E(D^-A^+)$. The C C bond is disubstituted ethanes (1 and 2) is an example for such a case. In this case, one can form two combinations out of D^+A^- and D^-A^+. With neglect of interfragmental overlap they are

$$\psi^+ = (2)^{-\frac{1}{2}}\{D^+A^- + D\ A^+\} \qquad (6)$$

$$\psi^- = (2)^{-\frac{1}{2}}\{D^-A\ - D^-A^+\}. \qquad (7)$$

Only ψ^- interacts with DA leading to the following expression for E_b.

$$Eb = \frac{1}{2}\{E(\psi^-) + E(DA) + \sqrt{[E(\psi^-) - E(DA)]^2 + 8h^2}\} - E(DA)_x + V_{nn}. \qquad (8)$$

In order to simplify this term, one has to evaluate the energies of ψ^+ and DA as a function of the R–X distance. When one does that (see Appendix 1 for details), one gets the following form for E_b:

$$E_b = \frac{1}{2}\{I - A + C_1 + \sqrt{(I - A + C_2)^2 + 8h^2}\} \qquad (9)$$

where I and A are the ionization potential and the electron affinity of the radical fragments ($I_R = I_X$, etc.). C_1 and C_2 reflect the difference of the various interactions (e.g., electron electron, nuclear–electron) within ψ^+ and DA, sometimes called the coulombic energy.[5] The difference in C_1 and C_2 arises from the fact that the former includes V_{nn}, while the latter does not (see Appendix 1 for details).

Hereafter we shall ignore in all our discussions the variations in C_1 and C_2, while making qualitative predictions about relative bond strengths within a certain family. Instead we shall focus attention on the variations of (I A) and h as our knowledge about them is more certain. Although this may not be always right to do, we find that this is necessary if we want to gain qualitative insight into the riddle. The fact that this approach appears to work does, in itself, provide justification for the strategy.

(b) A heteropolar bond such as C–Cl, for which at r_0 $E(DA) \leqslant E(D^+A^-) \ll E(D^-A^+)$. In this range, it is sufficient to interact DA with D^+A^- and to consider the effect of D^-A^+ as a perturbation on the resultant wave function. With neglect of D^-A^+, E_b reads

$$E_b = \frac{1}{2}\{E(DA) + E(D^-A^-) + \sqrt{[E(D^+A^-) - E(DA)]^2 + 4h^2}\} - E(DA)_x + V_{nn} \qquad (10)$$

which becomes

$$E_b = \frac{1}{2}\{I_R - A_X + C_1 + \sqrt{(I_R - A_X + C_2)^2 + 4h^2}\} \qquad (11)$$

and the various terms have the same meaning as before.

(c) A very polar or ionic bond such as Si–Cl, for which at r_0 $E(D^+A^-) < E(DA) \ll E(D^-A^+)$. In this case too, the expression for the bond energy takes the form in eqn (11). This region of the bond-polarity spectrum covers the so called super ionic bonds for which $E(D^+A^-) \ll E(DA)$.[5f] Thus, although D^+A^- lies below DA throughout this region, the bond will not be ionic in the practical sense of the word when the configurations lie close to each other and therefore mix appreciably.

In order to appreciate the operative value of the bond-polarity index, let us look at the following I_R-A_X values for various bonds.

R–X	I_R-A_X,eV[11]
H_3C–H	9.3
H_3C Cl	6.3
H_3Si Cl	~3.3
Na Cl	1.4

These values show that even at infinite R X separation the energy of D^+A^- approaches that of DA for Si–Cl and Na–Cl. Clearly at shorter distances the D^+A^- surface can actually cross the DA surface.

APPLICATIONS

Both eqns (9) and (11) show that if we neglect the variations in C_1 and C_2, then bond energy depends on two parameters; on the bond-polarity expressed by (I–A) and on the matrix element, h. How does bond energy vary as a function of these two parameters? One can gain insight into this problem by taking the derivatives of E_b in eqns (9) and (11). Doing that, one gets the following expressions for homopolar bonds and heteropolar bonds, respectively:

$$dE_b = \left\{ \frac{4h}{\sqrt{(I-A+C_2)^2 + 8h^2}} \right\} dh$$
$$+ \frac{1}{2}\left\{ 1 + \frac{(I-A+C_2)}{\sqrt{(I-A+C_2)^2 + 8h^2}} \right\} d(I-A)$$
$$(12)$$

$$dE_b = \left\{ \frac{2h}{\sqrt{(I_R-A_X+C_2)^2 + 4h^2}} \right\} dh$$
$$+ \frac{1}{2}\left\{ 1 + \frac{(I_R-A_X+C_2)}{\sqrt{(I_R-A_X+C_2)^2 + 4h^2}} \right\} d(I_X-A_R).$$
$$(13)$$

The first term in the brackets is always positive. Hence by making the matrix element more negative, i.e. dh < 0 and keeping (I − A) constant, the bond energy becomes more negative and according to our definition of E_b (eqn 5), the bond becomes stronger. Moreover, one can see that homopolar bonds (eqn 12) are more sensitive to variation of the matrix element, h, than are heteropolar bonds (eqn 13).

The second term in the brackets is also always positive even for homopolar bonds, since in eqn (12), $|(I − A + C_2)/\sqrt{(I − A + C_2)^2 + 8h^2}| < 1$. Hence, increasing the bond polarity, i.e. d(I − A) < 0 and keeping h constant, makes E_b more negative leading to a stronger bond. Moreover, very polar bonds for which $(I_R A_X + C_2) < 0$, and more sensitive to variation of

$(I_R − A_X)$, decreases, their bond strength increases quickly.

What happens then when the two variations oppose one another, i.e. when a decrease in (I–A) is accompanied by an increase in h (h becomes less negative)? The net effect of these two opposite trends will be determined by the ratio of the two partial derivatives of E_b (with respect to (I–A) and to h), i.e. the ratio of the two bracketed terms in eqns (12) and (13). Here, we must distinguish the homopolar from the very polar bonds, since as we have concluded before, the former are more sensitive to variations in h. Substituting representative values of h = − 5eV and I − A + C_2 = +7eV (e.g. see Appendix for C C) one gets for homopolar bonds

$$dE_b = 1.2674\,dh + 0.2782\,d(I–A). \qquad (14)$$

This means that homopolar bonds will be much more sensitive to variations in h than to variations in I-A. This difference in sensitivity increases as the value of |h| increases. Thus we conclude that in most cases, *homopolar bonds become weaker as the interaction matrix element becomes less negative, even if the (I–A) index decreases, i.e. homopolar bond strength is controlled by the matrix element.*

What is the chemistry behind this statement? Consider, for example, the bond strength along the series; C C, Si–Si, Ge Ge. Along this series, the I–A value decreases. At the same time h becomes less negative (eqn 5) since the I values of the atoms decrease in the order I(C) > I(Si) > I(Ge). Thus, one expects the bond energy to decrease along the series, and indeed one finds that the bond energies are 83, 53 and 45 kcal/mole respectively.[12]

Similar considerations can be applied to the C–H bond energies in the series H_3C-H, CH_3CH_2–H, $(CH_3)_2HC$–H, and $(CH_3)_3C$ H. As we move along this series the alkyl fragment becomes a better electron donor and I–A decreases. At the same time, |h| decreases also, because the orbital ϕ_R becomes more delocalized and less centered on the carbon causing S_{RX} to decrease (eqn 5). These variations are shown along with

R	X	I A,eV[11]	S_{RX}[13]	$|E_b|$,kcal/mole[12]
CH_3	H	9.3	0.614	104
C_2H_5	H	8.1	0.554	98
$(CH_3)_2CH$	H	7.2	0.535	95
$(CH_3)_3C$	H	6.7	0.514	92

experimental bond energies which reflect the expected decrease in bond strength upon increased substitution which leads to decrease of |h| (see Appendix 1 for the calculated values of these bond energies).

Let us now turn to the effect of opposite variation of h and (I_R-A_X) on the relative strengths of heteropolar bonds. We have already pointed out that these bonds are typically less sensitive than hompolar bonds to variations in h. Substituting representative values of I_R-A_X + C_2 = 3 eV (e.g. for C Cl) and h = − 5 ev into eqn (13) illustrates that:

$$dE_b = 0.9578\,dh + 0.3563\,d(I_R\ A_X) \qquad (15)$$

Therefore, we conclude that the *relative strength of heteropolar bonds, although still controlled by the matrix element h, will show a greater response than*
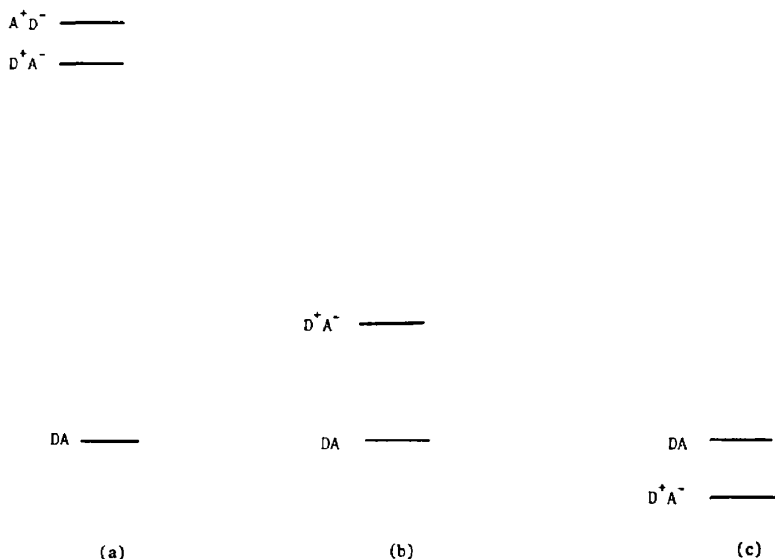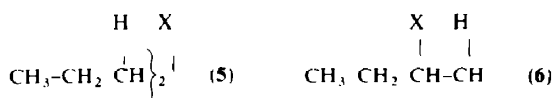
A^+D^- ———
D^+A^- ———

D^+A^- ———

DA ———   DA ———   DA ———

                                                     D^+A^- ———

(a)   (b)   (c)

Fig 1. Energy order of the bond configurations at r_0 in (a) a homopolar bond, (b) a heteropolar bond, (c) a very polar or ionic bond.

homopolar bonds to variations in (I_R-A_X). Thus, opposing variations of h and $(I_R A_X)$ will lead to smaller bond energy differences in the heteropolar series (see also calculations in Appendix 1).

This effect is illustrated nicely in Table 1 which lists the bond energies along the series R -X, where R is an alkyl group which varies from Me to tertiary Bu, and X = H, Me, F, OH, NH_2. It is evident that for the homopolar bonds (X = H, Me), the difference in bond strength between Me–X and Me_3 C–X (12 and 8 kcal/mole respectively) is significantly larger than that for the heteropolar bonds (X = F, Cl, OH, NH_2; $\leqslant 4$ kcal). Thus, the bond energies in the heteropolar series show a greater response to the polarity index (I_R-A_X).

Let us inspect the applicability of this rule to a slightly more subtle problem; the relative stability of the two isomers 3 and 4. The difference between the two is merely an exchange of the two labelled bonds, one being located on a primary carbon, the other on a secondary carbon. Thus the relative stability of the two isomers can be expressed as the difference in primary (1) and secondary (2) bond strengths; $\Delta E(4 \rightleftharpoons 3)$ = $E_{C\ Cl}(2) - E_{C\ Cl}(1) + E_{C-H}(1) - E_{C\ H}(2)$. Following the rules derived before, we conclude that iso-propyl chloride (3) should be more stable than n-propyl chloride (4) because the energy difference of a secondary and a primary C–H bond is expected to be larger than the same difference for the heteropolar primary and secondary C–Cl bonds. *Thus. in the competition between H and a better acceptor substituent over two different carbon sites, one being a better electron donor than the other, the hydrogen will prefer the worse donor (the least substituted) site.*

The heats of formation of C_3H_7X and C_4H_9X isomers given in Table 2, illustrates this generality. The iso-propyl isomers are more stable than the n-propyl isomers. A similar tendency is found for the butyl derivatives where the s-Bu isomer (6) is more stable than the n-Bu isomer (5) and the t-Bu isomer (8) is more stable than the iso-Bu isomer (7).

Cl   H
| |
CH_3CH-CH_2

3

H   Cl
| |
CH_3CH-CH_2

4

H   X
| |
CH_3-CH_2 $\overset{|}{CH}\}_2^|$ (5)

X   H
| |
$CH_3\ CH_2\ CH-CH$ (6)

H   X
| |
$CH_3\ C\ CH_2$ (7)
    |
   CH_3

X   H
| |
CH_3-C-CH_2 (8)
      |
    cglCH_3

Let us now turn to very polar or ionic bonds. Here, the I_R-A_X term is very low so that $(I_R-A_X + C_2)$ is negative. Consequently, the bond energies will be very sensitive to variations in $(I_R A_X)$. Using representative values of $I_R-A_X + C_2 = -1$ ev and h = -5 eV in eqn (13) we get

$$dE_b = 0.9950\,dh + 0.5498d(I_R-A_X). \qquad (16)$$

Thus, very polar or ionic bonds are much more sensitive than heteropolar and homopolar bonds to variations in (I_R-A_X). Subsequently one would expect in this case that bond strengths can increase with a decrease in (I_R-A_X).

A comparison of Si–X and C–X bond energies presented in Table 3 shows that for X = H, C, Si i.e. homopolar bonds, the C–X bonds having the higher matrix element $|h|$, are stronger than the Si–X bonds. On the other hand, for X = F, O, Cl, i.e. heteropolar or very polar bonds, the Si–X bonds are the stronger ones showing the response of the good electron acceptor

substituents to the better donor ability of Si. These results also indicate that the unusual strengths of the polar Si–X(X = F, O, Cl...) may originate from their essentially "ionic" nature (i.e. D^+A^- lies below DA, see Fig. 1).

CONCLUSION

Pauling stated years ago that the reaction $H_2 + F_2 \rightarrow 2HF$ is exothermic because the H–F bond has more ionic character and, therefore, is stronger than the average of an H H bond and a F–F bond. The

Table 1. C X bond strengths in R X compounds[a,b]

R	X					
	H	CH₃	F	Cl	OH	NH₂
CH₃	104	88	108	84	91	79
CH₂CH₃	98	85	106	81	91	78
CH(CH₃)₂	95	83	105	81	92	77
C(CH₃)₃	92	80	-	80	92	78

[a] Handbook of Chemistry and Physics, The Chemical Rubber Company, Cleveland Ohio, (1970).

[b] Units in kcals.

Table 2. Heats of formation of substituted propanes and butanes[a,b]

R·	X				
	NH₂	OH	F	Cl	SH
CH₃CH₂ĊH₂	-16.8	-61.2	-67.6	-31.0	-16.1
(CH₃)₂ĊH	-20.0	-65.1	-69.4	-33.6	-18.1
CH₃CH₂CH₂ĊH₂	-22.7	-65.8	-	-35.1	-21.0
CH₃CH₂ĊHCH₃	-25.4	-70.0	-	-38.6	-23.1
(CH₃)₂CHĊH₂	-	-67.8	-	-38.1	-23.2
(CH₃)₃Ċ·	-28.9	-74.7	-	-43.7	-26.1

[a] Units in kcals.

[b] J.D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, London (1970).

Table 3. Si–X and C X bond energies (kcal mole)[a]

Silicon Bond	Bond Energy	Carbon Bond	Bond Energy
Si-Si	53	C-Si	76
Si-C	76	C-C	83
Si-H	76	C-H	99
Si-O	108	C-O	86
Si-F	135	C-F	116
Si-Cl	91	C-Cl	81

[a] C. Eaborn, "Organosilicon Compounds", Butterworths, London (1960).

relationship between this fact and the greater stability of t-butyl fluoride relative to iso-butyl fluoride is not obvious. Using the LCFC method[5] we have reduced the complex interactions of these large molecules into two accessible components, the bond polarity index $(I_R \ A_X)$, and the matrix element, h.

The simplicity with which we use the LCFC approach restricts us to making qualitative rather than quantitive predictions. This is consistent with our general philosophy.[5] However, our equations lend themselves to quantitive predictions too, as is discussed in Appendix 1, and careful parametrizations of C_1 and C_2 for various bond types can reproduce quantitive trends quite nicely.

APPENDIX 1

Let us start with a 2×2 problem, which includes two configurations DA and ψ^+ (or $D^+ A^-$), having electronic energies H_{11} and H_{22} respectively at the equilibrium bond distance r_0. The lowest energy solution E_1, with inclusion of overlap, is given below (eqn 17). S_{12} is the overlap

$$E_1 = \frac{1}{2(1 - S_{12}^2)} \Big[H_{11} + H_{22} - 2H_{12}S_{12} + \sqrt{(H_{11} - H_{22})^2 - 4H_{11}H_{22}S_{12}^2 - 4H_{12}(H_{11} + H_{22}) S_{12} + 4H_{12}^2} \Big]$$

(17)

between the two configurations and H_{12} is their matrix element. The bond energy is the energy difference of E_1 and the energy of DA at infinite separation, $H_{11}(\infty)$ to which has been added the nuclear -nuclear repulsion at r_0, V_{nn}.

$$E_b = E_1 - H_{11}(\infty) + V_{nn}.$$

(18)

In order to simplify these terms into the forms given in the text, we must express everything in terms of the individual fragments and the various interactions of their MOs ϕ_R and ϕ_X.

Let us start with a homopolar case. The various expressions become:

$$H_{11} = \frac{1}{1 + S_{RX}^2} \{ \varepsilon_R + \varepsilon_X + 2V_{ne} + J_{RX} + K_{RX} + 2\beta_{RX} S_{RX} \}$$

(19)

$$H_{22} = \frac{1}{1 + S_{RX}^2} \{ \varepsilon_R + \varepsilon_X + 2V_{ne} + \tfrac{1}{2}J_{RR} + \tfrac{1}{2}J_{XX} + K_{RX} + 2\beta_{RX} S_{RX} \}$$

(20)

$$S_{12} = \frac{2S_{RX}}{1 + S_{RX}^2}$$

(21)

$$H_{12} = \frac{2}{1 + S_{RX}^2} \{ \beta_{RX} + (\varepsilon_R + V_{ne})S_{RX} + \langle \phi_R \phi_R | \frac{1}{r_{12}} | \phi_X \phi_R \rangle \}$$

(22)

$$H_{11}(\infty) = \varepsilon_R - \varepsilon_X.$$

(23)

In eqns (19)- (23), the ε's denote the orbital energies of ϕ_R and ϕ_X which are roughly equal in the homopolar case. V_{ne} is the electron nuclear attraction integral,[5c f] the various J's and K's are the electron electron repulsion integrals, S_{RX} is the MO overlap integral of ϕ_R and ϕ_X, while β_{RX} is the resonance integral of ϕ_R and ϕ_X with respect to the one electronic parts of the Hamiltonian.[5c f]

We wish now to express these equations in terms of the ionization potential I and the electron affinity, A. Within our approximation of one orbital per fragment, I and A are defined as

$$I_R = -\varepsilon_R \text{ or } I_X = -\varepsilon_X$$

(24)

$$A_R = -(\varepsilon_R - J_{RR}) \text{ or } A_X = -(\varepsilon_X + J_{XX})$$

(25)

Substituting these definitions into eqns (19) and (20) one gets that

$$H_{22} - H_{11} = I - A - \frac{1}{1 + S_{RX}^2} (S_{RX}^2 J_{RR} + J_{RX}).$$

(26)

The first term in eqn (26) is the difference of the ionization potential of one fragment and the electron affinity of the other and it is a positive quantity, estimating the energy cost of an electron transfer from one fragment to the other. The second term is negative, reflecting the smaller electron–electron repulsion in the ionic configuration, ψ^+. For illustrative purposes we have calculated the energy difference of these two configurations for H_2 using STO-3G values for the various integrals. The results listed below

r_{HH}, Å	$H_{22} - H_{11}$, eV
2	14.35
1.5	10.90
1.0	6.47
0.75	4.00

illustrate that indeed, as eqn (26) implies ψ^+ approaches DA in energy as r decreases owing to excess electrostatic stabilization. Let us denote this difference by C where $C < 0$. Thus, the energy of the ionic configuration will take the general form $E(\psi^+) = I \cdot A + C - F(S_{RX})^{5c}$ where $C < 0$, whereas, for the covalent configuration it will follow the general form $E(DA) = F(S_{RX})$, and their energy difference $E(\psi^+) - E(DA)$ will be $I \cdot A + C$. We can now substitute these expressions into eqns (17) and (18) and get the bond energies in terms of I, A and C. However, the equation is still very complex, since we do not neglect overlap. So, we wish to convert it to the simpler form of eqn (9) in the text. Let us see how this conversion is done. The first term within the square-root sign in eqn 17, after its division by $1 - S_{12}^2$, becomes

$$\left(\frac{H_{11} - H_{22}}{1 - S_{12}^2} \right)^2 = \left(I \ A + \frac{S_{12}^2 J_{RR} + C}{1 - S_{12}^2} \right)^2$$

and it can be converted to $(I-A + C_2)^2$. Similar treatment of the terms outside the square-root sign

$$\frac{H_{11} + H_{22} - 2H_{12}S_{12} + 2(1 - S_{12}^2)V_{nn} - 2(1 - S_{12}^2)H_{11}(\infty)}{1 - S_{12}^2}$$

gives

$$I - A + \frac{1}{1 - S_{12}^2} \{ S_{12}^2 J_{RR} + C + 2F(S) - 2H_{12}S_{12} + 2(1 - S_{12}^2)V_{nn} - 2(1 - S_{12}^2)H_{11}(\infty) \}$$

which can be expressed as $I \ A + C_1$. Finally, the other terms inside the square root sign can be written as $\sim 4H_{12}^2$ which can be further reduced to $8h^2$ using eqn (22), h is some effective resonance integral. All these manipulations taken together lead to the expression in eqn (9) in the text, which contains three experimentally unknown parameters: C_1, C_2 and h.

Similar treatment of the heteropolar case leads to a similar expression, only now the matrix element H_{12} is smaller by a factor of $\sqrt{2}$.[9]

In this way, the entire problem is reduced to a discussion of bond energies in terms of the ionization potentials, electron affinities, and the resonance integral of the two singly occupied orbitals of the fragments constituting the bond.

We have also tested the potentiality of these equations for calculating bond energies. We have calculated the bond energy of H_2 from the DA-ψ^- interaction using STO-3G integrals in the equilibrium distance of H_2. This gave us $|E_b| = 128.16$ kcal/mole. We have calculated each term in the explicit eqns (17) and (18) and equated them with the various terms in eqns (9) and (5), using experimental values for I and

A. These led to the following values:

$C_1 = +1$ eV
$C_2 = -5$ eV
$k \simeq -0.95$ (i.e. $h = -8.44$ eV, see eqn 5)

Using these values, the bond energy we get is $|E_b|$ = 129.6 kcal/mole (eqn 9). These parameters were used to calculate C—H bond energies and we get the following results:

$$CH_3–H \quad 111 \text{ kcal/mole}$$
$$C_2H_5–H \quad 91 \text{ kcal/mole}$$

Repeating this procedure and treating H_2 as a heteropolar bond (i.e. interacting only one ionic configuration with the covalent configuration) we get the following parameters

$$C_1 \approx -5 \text{ eV}$$
$$C_2 \approx -2 \text{ eV}$$
$$k \approx -1.2$$

Using these parameters to calculate C–F bond energies we get:

$$CH_3–F \quad 115 \text{ kcal/mole}$$
$$C_2H_5–F \quad 108 \text{ kcal/mole}$$
$$(CH_3)_2CH–F \quad 109 \text{ kcal/mole}$$

We have used different parametrizations for h with the same result that the difference in C–F bond strengths is smaller than that of the corresponding C–H bonds (for discussion see text). Moreover, the C–F bonds are much less sensitive to the decrease of $|h|$.

We have tried these sets of parameters for all bond types. The numerical results are only fair, but most of the qualitative trends are reproduced. These parameters underestimate bonds with small overlap values (e.g., C—C) but overestimate bonds having high overlap values (e.g., Si–H). Thus, we have calculated the H_2 molecule using STO-3G integrals at various H–H separations. It turns out that while k varies just a little, C_1 and C_2 vary substantially and for overlaps $\leqslant 0.5$ one should use $C_1 = -5$ eV, $C_2 = -2$ eV in order to get reasonable numerical results. For example, using these values, one gets 92 kcal/mole and 88 kcal/mole for H_3C—CH_3 and H_3C–SiH_3 respectively. It is obvious therefore, that only two sets of parameters for all bond types are insufficient to reproduce the experimental bond energies. Quantitative predictions across the board would only be attainable by careful parametrization of C_1 and C_2.

REFERENCES

[1a] University of Washington; [b] Ben-Gurion University.
[2a] L. Pauling, The Nature of the Chemical Bond. Cornell University Press, Ithaca, New York (1960); [b] L. Pauling and J. Sherman, J. Am. Chem. Soc. 59, 1450 (1937); [c] L. Pauling, Ibid. 53, 1367 (1931)
[3] J. C. Slater, Phys. Rev. 38, 1109 (1931).
[4a] R. S. Mulliken, J. Am. Chem. Soc. 72, 4493 (1950); [b] R. S. Mulliken, J. Chem. Phys 19, 900 (1951); [c] R. S. Mulliken, Ibid. 56, 295 (1952).
[5a] N. D. Epiotis, Angew. Chem. Int. Ed. Engl. 13, 751 (1974), [b] N. D. Epiotis and S. Shaik, J. Am. Chem. Soc. 99, 4936 (1977); [c] N. D. Epiotis and S. Shaik, Ibid.100, 1, 9, 29 (1978), [d] S. Shaik and N. D Epiotis, Ibid.100, 18 (1978); [e] N. D. Epiotis, S. Shaik and W. Zander, Rearrangements in Ground and Excited States edited by P. de Mayo. Academic Press, New York (1979); [f] N. D. Epiotis, Theory of Organic Reactions. Springer-Verlag, New York (1978).
[6a] N. D. Epiotis, J. R. Larson, R. L. Yates, W. R. Cherry, S. Shaik and F. Bernardi, J. Am. Chem. Soc. 99, 7460 (1977); [b] N. D. Epiotis, W. R. Cherry, S. Shaik, R. L. Yates and F. Bernardi, Topics Curr. Chem. 70,(1977).
[7] These are the diradical states comprising a bond. For a lucid discussion see, L. Salem and C Rowland, Angew. Chem. Int. Ed. Engl. 11, 92 (1972).
[8] For example, if one considers the D^-A^- D^*A^* interaction in the $CH_3 \Leftrightarrow NH_2$ union in CH_3NH_2, one finds that the mixing is proportional to the overlap of the lone pair of N with an antibonding orbital of CH_3 having the same symmetry. This is a π-conjugative effect which is usually small in comparison with the mixing of DA with D^+A^- and which is responsible for the so-called C—N σ bond.
[9] Rules for taking matrix elements between configurations can be found inter alia in, S. P. McGlynn, L. G. Vanquickenborne, M. Kinoshita and D. G. Carroll, Introduction to Applied Quantum Chemistry. Holt, Rinehart and Winston, New York (1972).
[10a] R. Hoffman, J. Chem. Phys. 39, 1397 (1963); [b] ibid.40, 2474 (1963). This is not the only form, and one can use for h other scales which reflect the nature of R and X. For example, a CNDO type matrix element is acceptable too. We wish to emphasize that the choice of the matrix element does not affect the trends discussed in the text.
[11] V. I. Vedeneyev, L. V. Gurvich, V. N. Kondvatyev, V. A. Medvedev and Y. L. Frankevich, Bond Energies, Ionization Potentials and Electron Affinities St. Martin's Press, New York (1966)
[12] Handbook of Chemistry and Physics. The Chemical Rubber Co., Cleveland, Ohio (1970).
[13] The overlap values were obtained using Slater Type orbitals and Extended Hückel coefficients for the ϕ_R and ϕ_X orbitals.