Additivity of Bond Energies in the Light of the Maximum Overlap Approximation (MOA) and MINDO/3*

Michael J. S. Dewar, Donald H. Lo**, and Zvonimir B. Maksic***

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, USA

Received November 19, 1973

Optimum parameters are determined for the use of the maximum overlap approximation (MOA) to calculate heats of atomization of a varied set of eleven hydrocarbons. The agreement with experiment is generally good. The reasons for this success are discussed in terms of an analysis by energy partitioning of MINDO/3 calculations for the same hydrocarbons.

INTRODUCTION

While the majority of quantum mechanical calculations in recent years have made use of the molecular orbital (MO) approach, the valence bond (VB) method still has a number of attractions, particularly for the treatment of molecules with »localized« bonds. The VB picture is certainly much closer to the conventional intuitive one in which the bonding in such molecules is represented in terms of two-center bonds formed by sharing of pairs of electrons. There has therefore been a revival of interest recently in VB methods, in particular the simple variant known as the maximum overlap approximation (MOA) which has recently been applied to a large number of hydrocarbons1.

In the MOA method the hybridization of the AOs used to form two-center bonds is chosen to ensure the maximum overall overlap between the corresponding pairs of AOs in the molecule as a whole. It has been shown1,2 that the corresponding hybridization parameters can be used successfully to correlate a number of molecular properties in unconjugated hydrocarbons, e.g. p.m.r. chemical shifts, n.m.r. coupling constants (J_{CC} and J_{CH}), thermodynamic acidities, and CH stretching frequencies. The overlap integrals between the pairs of AOs used to form bonds have also been correlated with the corresponding bond lengths3 and bond energies4.

Although this simple and attractive approach has thus proved remarkably successful, its basis has been essentially intuitive and empirical. It therefore seemed to us of interest to see if a satisfactory theoretical explanation could be given for its success. We also wanted to see how well the MOA method

---

* This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and the Robert A. Welch Foundation through Grant F-126.
** Present address: Erie County Laboratory, 462 Grider Street, Buffalo, New York 14215.
*** Robert A. Welch Postdoctoral Fellow, 1971—2. On leave of absence from Institute »Ruder Bošković«, Zagreb, Croatia, Yugoslavia.
could reproduce heats of formation on the assumption that bond energies are related in the manner indicated above to orbital overlap.

An obvious approach seemed to be to compare the results of MOA calculations for hydrocarbons with those from the MINDO/3 method. MINDO/3 is a SCF method, based on the latest version of the MINDO/6 semiempirical SCF MO treatment, equivalent to the INDO method of Pople et al. but parametrized to reproduce ground state properties of molecules rather than to mimic the results of ab initio SCF calculations. It has two major advantages for the present purpose. First, it gives good estimates of the heats of atomization of molecules. Secondly, the expression for the total energy of a molecule can be dissected into terms representing contributions by individual atoms and bonds by using the Fischer-Kollmar technique of energy partitioning.

THEORETICAL APPROACH

Since our concern was with the possible use of the MOA method for calculating heats of atomization, we calculated the hybridization parameters by a procedure that is somewhat different from that used previously.

We assumed that the bond energy of a given bond in a molecule, i.e. the corresponding contribution to the heat of atomization \( \Delta H_a \), is a linear function of the corresponding overlap integral \( S_{ij} \). Thus the bond energy \( E_{ij}^{CC} \) of a bond between two carbon atoms, formed by interaction of two hybrid AOs \( \Phi_i \) and \( \Phi_j \), is given by

\[
E_{ij}^{CC} = k_{CC} S_{ij} + L_{CC}
\]

(1)

where \( k_{CC} \) and \( L_{CC} \) are constants. Likewise for CH bonds.

\[
E_{kl}^{CH} = k_{CH} S_{kl} + L_{CH}
\]

(2)

The heat of atomization is then given by:

\[
\Delta H_a = k_{CC} \sum_i S_{ij} + k_{CH} \sum_k S_{kl} + N_{CC} L_{CC} + N_{CH} L_{CH}
\]

(3)

where the first sum is over the \( N_{CC} \) CC bonds and the second over the \( N_{CH} \) CH bonds. The AOs are to be chosen in such a way as to minimize the energy of the molecule, i.e. to maximize \( \Delta H_a \).

The individual atomic orbitals \( \Phi_i \) of atom m are written as hybrids of corresponding s and p AOs:

\[
\Phi_i = a_i s_m + (1 - a_i^2)^{1/2} p_{mi}
\]

(4)

where \( s_m \) is the s AO of atom m while \( p_{mi} \) a corresponding p AO with its axis along that of the hybrid AO \( \Phi_i \). \( a_i \) is the parameter which determines the hybridization of \( \Phi_i \). In the case of a hydrogen atom, \( a_i \) is of course unity. The AOs of a given atom are required to be orthogonal. Thus if \( \Phi_i \) and \( \Phi_j \) are two hybrid AOs of atom m

\[
\langle \Phi_i | \Phi_j \rangle = a_i a_j + (1 - a_i^2)^{1/2} (1 - a_j^2)^{1/2} \cos \theta_{ij} = 0
\]

(5)

where \( \theta_{ij} \) is the interaxial angle between the p AOs \( \Phi_i \) and \( \Phi_j \).

The overlap integrals in equation (2) are calculated using Slater-Zener AOs. Here a problem arises because it is well known that the optimum orbital exponents are not the same for orbitals in free atoms as for the
corresponding orbitals in atoms that are chemically combined. In the latter case it is also necessary to distinguish between p AOs used to form σ bonds and those used to form π bonds. In the case of hydrocarbons there are four exponents to be determined; that for hydrogen (ζ_H), that for carbon 2s (ζ_Cs), that for carbon 2p used in a σ bond (ζ_Cs) and that for carbon 2p used in a π bond (ζ_Cp).

The heat of atomization of a hydrocarbon is therefore a function of the hybridization parameters of the various carbon atoms (a_i in equation (4)), the quantities K_CC, L_CC, K_CH, and L_CH in equation (3), and the orbital exponents ζ_H, ζ_Cs, ζ_Cp, and ζ_Cp.

The values of the parameters were determined in the following way, using a set of hydrocarbons whose geometries and heats of atomization are known experimentally. Assuming the molecule to have the observed geometry, and assuming values for the various parameters, we can calculate a corresponding heat of atomization (E_μ) for each molecule μ using equation (3). If the corresponding experimental value is ΔH_μa, the error in our estimate is (E_μ - ΔH_μa). The parameters are chosen to minimize the sum (F) of the squares of the errors,

$$ F = \sum \left( E_\mu - \Delta H_\mu a \right)^2 $$

(6)

In practice we assumed values for ζ_H and determined the others by minimizing F with respect to the other parameters by the SIMPLEX method. The results for various values of ζ_H are listed in Table I. The optimum value

| TABLE I |
| Optimized MOA Parameters for Hydrocarbons |

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Orbital exponent (ζ_H) for hydrogen</th>
<th>Slatera</th>
<th>C.-R. b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.0</td>
<td>1.1</td>
<td>1.2</td>
</tr>
<tr>
<td>ζ_s2t</td>
<td>1.8552</td>
<td>1.8641</td>
<td>1.9056</td>
</tr>
<tr>
<td>ζ_s2p</td>
<td>1.3429</td>
<td>1.3399</td>
<td>1.3877</td>
</tr>
<tr>
<td>ζ_s2p</td>
<td>1.4420</td>
<td>1.4476</td>
<td>1.5147</td>
</tr>
<tr>
<td>K_CH kcal mol⁻¹</td>
<td>124.3790</td>
<td>124.6198</td>
<td>129.7255</td>
</tr>
<tr>
<td>L_CH kcal mol⁻¹</td>
<td>-5.2594</td>
<td>-4.9222</td>
<td>-5.3480</td>
</tr>
<tr>
<td>K_CC kcal mol⁻¹</td>
<td>117.4559</td>
<td>119.9258</td>
<td>121.5427</td>
</tr>
<tr>
<td>L_CC kcal mol⁻¹</td>
<td>19.2780</td>
<td>17.7197</td>
<td>19.3773</td>
</tr>
<tr>
<td>SD kcal mol⁻¹</td>
<td>3.09</td>
<td>2.98</td>
<td>2.92</td>
</tr>
</tbody>
</table>

(2) Slater exponents except ζ_H = 1.2
(3) Clementi-Raimondi exponents except ζ_H = 1.2
(4) Values used for the calculations in Table II
(d) Standard deviation of calculated ΔH_a from observed ΔH_a for the hydrocarbons listed in Table II, except cyclobutene and cyclopentane
for \( \bar{c}_H \) is clearly near 1.3. For comparison, values are also listed for standard Slater exponents\(^{10} \) and for the modified exponents recommended by Clementi and Raimondi\(^ {11} \). The results indicate very clearly the need for using different exponents for free atoms and for atoms in molecules and also indicate that little is gained by using the Clementi-Raimondi exponents in place of Slater ones.

**RESULTS AND DISCUSSION**

Table II shows the optimum MOA estimates of heats of atomization for the chosen set of eleven hydrocarbons. It will be seen that the agreement is quite close for most of them; note in particular the good results for ethane, ethylene, and acetylene, implying that the MOA approximation holds for bonds of all types from single to triple, and for cyclopropane and cubane, both highly strained compounds. On the other hand the errors are larger for two of the eleven compounds (cyclobutene; error, \(-14.8 \text{ kcal/mol}\); and cyclopentane; error, \(-29.2 \text{ kcal/mol}\)). Evidently the parallel between overlap integrals and bond energies is not at all universal. On the contrary it seems liable to break down for no obvious reason, neither cyclobutene nor cyclopentane possessing features that are absent in the other nine hydrocarbons.

**TABLE II**

*Calculated and Observed Heats of Atomization of Hydrocarbons*

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Heat of atomization (( \Delta H_a/\text{kcal mol}^{-1} )) at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed</td>
</tr>
<tr>
<td>Methane</td>
<td>397.8</td>
</tr>
<tr>
<td>Ethane</td>
<td>674.6</td>
</tr>
<tr>
<td>Propane</td>
<td>954.3</td>
</tr>
<tr>
<td>Ethylene</td>
<td>537.7</td>
</tr>
<tr>
<td>Propene</td>
<td>820.4</td>
</tr>
<tr>
<td>Acetylene</td>
<td>391.8</td>
</tr>
<tr>
<td>Cyclopropane</td>
<td>812.5</td>
</tr>
<tr>
<td>Cyclobutane</td>
<td>1094.0</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>1393.9</td>
</tr>
<tr>
<td>Cyclobutene</td>
<td>958.7</td>
</tr>
<tr>
<td>Cubane</td>
<td>1635.2</td>
</tr>
</tbody>
</table>

We have included in Table II heats of atomization given by MINDO/3. In MINDO/3 calculations the geometry is normally calculated by minimizing the energy with respect to all geometrical variables. Here, however, we are concerned with a comparison of MOA with MINDO/3; to facilitate this we have used experimental geometries in both cases. The errors in the MINDO/3 energies are consequently somewhat larger than usual, the heats of atomization tending to be too small.

In an all-valence-electron MO approximation, the total energy \( E_T \) of a molecule is given by

\[
E_T = E_{el} + E_{nn}
\]

(7)

where \( E_{el} \) is the total electronic energy and \( E_{nn} \) is the total core-core repulsion energy. The heat of atomization, \( \Delta H_a \), is then given by

\[
\Delta H_a = - [E_T - \Sigma E_A]
\]

(8)

* 1 kcal = 4.184 kJ
where $E_A$ is the total energy of atom A and the sum is over all the atoms that compose the molecule we are considering. In an approximation of the MINDO type, where electron repulsion integrals involving bicentric overlap are neglected, this can be expanded following the energy partitioning scheme of Fischer and Kollmar:

$$\Delta H_a = T_1 + T_2 + T_3$$  (9)

where

$$T_1 = -\sum_{A<B} \left( E_{AB}^R + E_{AB}^V + E_{AB}^J + E_{AB}^K + E_{AB}^N \right)$$  (10)

$$T_2 = -\sum_{A<B} \left( E_{AB}^R + E_{AB}^V + E_{AB}^J + E_{AB}^K + E_{AB}^N \right)$$  (11)

$$T_3 = -\sum_A \left( E_A^U + E_A^R + E_A^K - E_A \right)$$  (12)

Here $\sum$ implies summation over pairs of adjacent atoms i.e. ones that are directly bonded to one another, while $\sum$ implies summation over nonadjacent pairs. Thus $T_1$ represents the contribution to $\Delta H_a$ of interactions between atoms in forming bonds, $T_2$ the corresponding nonbonded interactions, and $T_3$ the changes in energies of atoms, through promotion or transfer of electrons from one atom to another. $E_{AB}^R$ denotes one-electron terms, i.e. those involving the one-electron core resonance integrals $\beta_{ij}$ between AOs of atoms A and B. $E_{AB}^V$ is the core-electron attraction between atoms A and B, i.e. a sum of the attractive potential energies between the valence electrons of A and the core of B and between the valence electrons of B and the core of A. $E_{AB}^J$ and $E_{AB}^K$ are the coulombic and exchange interactions between the valence electrons of A and those of B. $E_{AB}^N$ is the A—B core repulsion. $E_A^U$ is the sum of the monocentric kinetic energy of the valence electrons of atom A and the attraction between them and the core of atom A. $E_A^R$ and $E_A^K$ are the coulombic and exchange interactions between the valence electrons of atom A. All these quantities can be calculated very simply for the MINDO wave function. The success of the MINDO/3 method suggests that the dissection of $\Delta H_a$ into one center, bonded two-center, and nonbonded two-center terms is probably meaningful.

The well known additivity of bond energies in unconjugated molecules implies that $\Delta H_a$ can be dissected into bonded two-center contributions. The success of the MOA method implied further that the corresponding bond energies $E_{xy}$ between pairs of atoms X and Y can be expressed in the form (see equation (11)):

$$E_{xy} = K_{xy} \sum S_{ij} + nL_{xy}$$  (13)

where the sum is over the $n$ pairs of AOs $\Phi_i$ and $\Phi_j$ used in forming the $n$ bonds between atoms X and Y.

The simplest and intuitively most reasonable quantity to identify with bonding is the nearest-neighbor two-center term $T_1$ in equation (9). There
is indeed quite a good linear relation between $T_1$ and the experimentally determined heat of atomization $\Delta H_a$ (Figure 1). Indeed the least squared line through the points in Figure 1 passes through the origin. The slope of the line ($-1.698$) is, however, far from unity. A large part of the bonding must therefore be attributed to the other terms ($T_2 + T_3$). If therefore $T_1$ is a measure of bonding, so must also be ($T_2 + T_3$). There should therefore be a linear relation between $T_1$ and ($T_2 + T_3$) and this indeed is the case (Figure 2).

There is, however, a complication. Although the plots in Figures 1 and 2 look nicely linear, the standard deviations of the points for the best straight lines are in fact very large in a chemical sense (SD for $\Delta H_a$, 2.65 eV; SD for $T_1$, 3.80 eV). Since MINDO/3 gives heats of atomization that are usually correct to 0.3 eV, it is clear that there must be a remarkable cancellation of the deviations of $T_1$ with those of ($T_2 + T_3$).

A further curious point is that the success of the MOA method indicates that $\Delta H_a$ is linearly related to the bond overlap integrals. Now according to the Mulliken approximation used in MINDO/3, these in turn are proportional to the one-electron core resonance integrals. It follows that $\Delta H_a$ is linearly related not to $T_1$ but to the one-electron terms in $T_1$. The deviations from linearity in Figure 1 are due to fluctuations in the two-center terms in $T_1$ which cancel with analogous fluctuations in ($T_2 + T_3$).

This of course is in full agreement with the deduction by Ruedenberg that chemical bonding is essentially a function of the one-electron exchange terms. Our analysis suggests a further refinement of this picture. If atoms behaved classically, chemical bonding would be virtually nonexistent. The electron distribution in a set of isolated atoms is such as to minimize their
total energy. When the atoms come together, the resulting change in energy can be dissected into a »classical« part corresponding to simple electrostatic interactions and a »nonclassical« part corresponding to the interference effects of orbitals that lead to changes in the one-electron terms. Since the overall change in energy of a set of atoms on combination to form a molecule is only a small fraction of the total energy, the perturbation involved is quite small. Since the classical electrostatic interactions should have a first order effect on the electron distribution but only a second order effect on the energy, their overall contribution to the latter should be small. If, however, we dissect this contribution into individual one-center and two-center interactions, the latter may well be large since they depend on local changes in electron distribution. If added together, however, they must nearly cancel. Thus we can relate bonding energy to the one-electron two-center terms only, i.e. those involving the core resonance integrals $\beta_{ij}^C$, or to the total energy, including all terms, but we cannot relate it to any intermediate dissection. This is probably why the Extended Hückel (Wolfberg-Helmholz) method gives such poor results. In it one tries to identify bonding with a combination of one-center terms and two-center exchange terms. As Figures 1 and 2 indicate, hybrid treatments of this kind may well give results that show general linear correlations with experiment but they cannot be expected to give quantitative results with chemical accuracy.

REFERENCES