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BOND ENERGIES, VALENCE STATE ENERGIES AND RESONANCE[1,2]

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BOND ENERGIES, VALENCE STATE ENERGIES AND RESONANCE[1,2]

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[1] Part I: G. R. Somayajulu, J. Chem. Phys. 31, 919 (1959).

[2] Part II: G. R. Somayajulu, submitted for publication.

In order to evaluate the effects of resonance (both π-electron and ionic-covalent) on the heats of atomization of molecules, bond energies have been estimated on the basis of the relation: $k_e r_e^2/E$ = const. applicable for bonds of any type and of any order between two given atoms, and on the basis of the valence state energies of the atoms. The valence state energy of an atom is defined as that part of the heat of atomization of the molecule that can be attributed to the atom in a state corresponding to the state of hybridization in the molecule. For the formation of the molecule from the atoms in their valence states (not necessarily spectroscopic states) the energy given off is the sum of the valence state energies, which is equal to the total heat of atomization. An assumption is made that the valence state energy of hydrogen in homologous compounds is constant, being equal to its standard heat of formation; this has facilitated the derivation of the valence state energies of the other

atoms in the homologous compounds. On the basis of the valence state energies of certain standard atoms, viz., primary, secondary, tertiary, quaternary, trigonal, and digonal carbon atoms, hydrogen, etc., the expected heats of atomization of several conjugated and hyperconjugated molecules have been determined. If resonance were to be important, the observed heat of atomization of a molecule would be higher than its expected value by an amount called the stabilization energy. Thus the stabilization energy of benzene is 19.56 kcal/mole at $0^{\circ}K$. However, for a number of classical hydrocarbon molecules, the stabilization energies are all negative indicating no resonance. Alkylation has been found to lower the stabilization energies of ethylene, benzene, and acetylene but increases those of formaldehyde, formic acid, formamide, etc. Thus in classical hydrocarbon molecules containing non-hydrocarbon groups, there seems to be evidence in favor of resonance.

It has been suggested that the strengths of heteropolar bonds, explained by Pauling on the basis of ionic-covalent resonance, may be explained in terms of the strengths of the hybrid orbitals.

1. INTRODUCTION

Previous attempts[3-7] to interpret chemical structure in terms of

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[3] G. W. Wheland, Resonance in Organic Chemistry (John Wiley & Sons, Inc., New York, 1955).

[4] J. W. Baker, Hyperconjugation (Clarendon Press, Oxford, England, 1952).

[5] R. S. Mulliken, C. A. Rieke, and W. G. Brown, J. Am. Chem. Soc. 63, 41(1939).

[6] R. S. Mulliken, Tetrahedron 5, 253 (1959); 6, 68 (1959).

[7] L. Pauling, The Nature of the Chemical Bond, 3rd ed. (Cornell University Press, Ithaca, New York, 1960).

π-electron resonance have been recently criticised[1,8,9]. A reinterpretation

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[8] M. J. S. Dewar and H. N. Schmeising, Tetrahedron 5, 168 (1959).

[9] M. G. Brown, Trans. Faraday Soc. 55, 694 (1959).

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of the lengths of the C-C bonds in terms of orbital radii has not revealed any effects of π-electron resonance in the ground states of classical[10] molecules such as 1,3-butadiene, methyl acetylene, etc. Even in a non-classical

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[10] Following Dewar and Schmeising, we define a classical molecule as one for which only a single classical (unexcited) structure can be written. If the molecule cannot be represented by one classical structure, we call such molecule non-classical.

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molecule such as benzene, resonance shortening of the CC bond is only

0.016 A. An analysis of the lengths in benzene derivations has also shown the effects of resonance to be negligible for some derivatives[11]. It has

[11] J. Trotter, Tetrahedron 8, 13 (1960).

been also found[12] possible to interpret the force constants of the C-C bonds

[12] G. R. Somayajulu, J. Chem. Phys. 28, 814 (1958).

in terms of the strengths of the hybrid orbitals. If the lengths and force constants of the C-C bonds vary with hybridization, so also must their bond energies. If resonance is not important in classical molecules, the heat of atomization of a classical molecule must be given by the sum of either the energies of the bonds or the contributions of the atoms present in it. To test this theory, we have estimated the contributions of some standard carbon atoms, viz., primary, secondary, tertiary, quaternary, trigonal, and digonal carbon atoms. The contribution of hydrogen has been assumed to be constant in various homologous compounds, being given by one-half of the dissociation energy of H_2. We have also estimated the contributions of some standard N, O, and S atoms. Based on these values, we have estimated the heats of atomization of several conjugated and hyperconjugated molecules, and found little evidence in favor of resonance in classical hydrocarbons such as 1,3-butadiene, propene, etc., but the molecules such as acetic acid, acetaldehyde, acetone, acetamide, etc., show evidence of stabilization due to resonance or some other factor.

We have also estimated[13] the energies of various types of CC, CH,

[13] While this paper was about to be submitted for publication, we saw a paper by M. J. S. Dewar and H. N. Schmeising, Tetrahedron 11, 96 (1960) in which they have also estimated the energies of various types of CC and CH bonds. However, while we used a relationship between force constant, bond lenght and bond energy, Dewar and Schmeising used a relationship between bond length and bond energy. The results obtained through these two methods have been found to be different. In Section 3 we have presented arguments to show that bond energies based solely on any relationship between bond length and bond energy are not expected to be reliable.

CN, CO and CS bonds. Some of these have been estimated on the basis of a relationship between force constant, bond length and bond energy.

As a first approximation, we have assumed the energies of the C-C bonds formed through the pairing of non-identical atomic orbitals to be sums of the orbital strengths[14]. However, since the orbitals which differ

[14] One-half of the energy of an sp^3-sp^3 bond is taken as a measure of the strength of the sp^3 orbital; similarly for sp^2 and sp orbitals. Alternatively, we may assume the strength of a bond to be given by the product of the orbital strengths. Such an assumption seems to be desirable for treating the strengths of the alkali hydrides and a number of other molecules.

in percentage s-character also differ in electronegativity,[1,6,15] according

[15] A. D. Walsh, Trans. Faraday Soc. 43, 60 (1947).

to the concept of ionic-covalent resonance, a bond such as sp^2-sp^3 is expected to be stronger than indicated by the strengths of the sp^2 and sp^3 orbitals. That such is not the case has been verified by us; the bond energies of such bonds in various molecules being either equal to or less than the calculated values. We have previously[2] pointed out that when one takes changes in the bonding orbitals through hybridization into account, it is illogical to expect a heteropolar bond to be stronger than indicated by the strengths of the appropriate orbitals used in the bond formation. This may be understood more clearly from the following:

There are several hints in the literature[16] that the enhanced strength

[16] See M. G. Brown, Trans. Faraday Soc. 55, 9 (1959) and the references cited therein.

of a heteropolar diatom such as HF, when compared with the strengths of the homopolar H_2 and F_2, is due to the reorganization of the valence state of the fluorine atom. It is equivalent to saying that the dissociation energy of HF is given by the sum of the valence state energies of H and F (reorganized). Why the valence state of the fluorine atom undergoes reorganization may be understood from the standpoint of the repulsive forces operating in HF and F_2. If the natural tendency of an atom is to use its strongest orbital

for bonding, this tendency is opposed by the repulsive forces of the type postulated by Pitzer[17]. The valence shell - valence shell repulsion

[17] K. S. Pitzer, J. Am. Chem. Soc. 48, 2140 (1948).

presumably does not allow fluorine to use an orbital stronger than p in F_2, whereas the absence of such repulsion in HF, allows fluorine to use an orbital considerably stronger than p[18]. Since the electronegativity

[18] Absence of such valence shell - valence shell repulsion in Cl_2 similarly permits chlorine to use an orbital considerably stronger than p for bonding; this may explain why the dissociation energy of Cl_2 is greater than that of F_2.

of an orbital (as defined by Mulliken[19]) depends on the strength of the

[19] R. S. Mulliken, J. Chem. Phys. 2, 782 (1933); 3, 573 (1935).

orbital, fluorine will be more electronegative in HF than in F_2. If we assume the orbital strength itself to be a measure of the orbital electronegativity, then the energy necessary for the reorganization of the valence state of the fluorine atom will be equal to the difference in the energies of the fluorine atoms in the two valence states. Pauling[7], on the other hand, treats the electronegativity of fluorine to be constant in both F_2 and HF and assumes that the difference in the electronegativities of H

and F strengthens the bonding in HF. Since Pauling's approach is completely different from ours, these two approaches should not be mixed.

2. SYMBOLS AND DATA

ΔH_f = heat of formation of a gaseous compound from its constituent atoms in their standard states.

ΔH_A = heat of atomization of a gaseous compound into its constituent atoms in the gaseous state.

D = dissociation energy of a diatomic molecule or of a bond in a polyatomic molecule.

E = energy of a bond; the sum of energies of all the bonds in a molecule gives its heat of atomization.

V = valence state energy of an atom; the sum of the valence state energies of all atoms in a molecule gives its heat of atomization.

S = strength of an orbital; the sum of the strengths of all the bonding orbitals of an atom gives its valence state energy; also the sum of the strengths of the bonding orbitals of a bond gives the bond energy.

k_e = bond stretching force constant from the zeroth order frequencies.

k_o = bond stretching force constant from the observed frequencies.

r_e = equilibrium internuclear distance.

r_o = internuclear distance in the vibrational ground state of a molecule.

If not mentioned otherwise, the heats of formation of the compounds treated in this paper are from Rossini et al.[20,21], the bond lengths from

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[20] F. D. Rossini et al., American Petroleum Institute Research Project 44 (Carnegie Press, Pittsburgh, Pennsylvania, 1953).

[21] F. D. Rossini et al., National Bureau of Standards Circ. No. 500 (1952).

Sutton[22] and the force constants from Cottrell[23]. The values of ΔH_f,

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[22] L. E. Sutton, Tables of Interatomic Distances and Configuration in Molecules and Ions (The Chemical Society, London, England, 1958).

[23] T. L. Cottrell, The Strengths of Chemical Bonds, 2nd ed. (Butterworths Scientific Publications, London, England, 1958).

ΔH_A, D, E and S are in kcal/mole, k_e and k_o in md/A and r_e and r_o in A. If not mentioned otherwise, all the thermodynamic quantities quoted in the text refer to 0^oK and are without the inclusion of the zero point energy. For ready reference, the heats of formation of some gaseous atoms from their reference states have been given in Table I.

3. METHODS OF ESTIMATION OF BOND ENERGIES

Excepting in a few simple cases, there are no unambiguous methods for the estimation of the energies of bonds in polyatomic molecules. Since the force constant and bond length are also measures of bond strength[12,15,23,24]

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[24] M. Szwarc and M. Evans, J. Chem. Phys. 18, 615 (1950).

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attempts to use them for the prediction of the bond energies have been made by several authors[25-32]. We have shown[32] recently that the force constant,

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[25] J. J. Fox and A. E. Martin, J. Chem. Soc. 884 (1939).

[26] H. A. Skinner, Trans. Faraday Soc. 41, 645 (1945).

[27] E. C. Baughan, Trans. Faraday Soc. 44, 845 (1948).

[28] A. D. Walsh, J. Chem. Soc. 331 (1948).

[29] G.Glockler, J. Chem. Phys. 19, 124 (1951); J. Phys. Chem. 61, 31 (1957); 62, 1049 (1958).

[30] E. R. Lippincott and R. Schroeder, J. Chem. Phys. 23, 1131 (1955); J. Am. Chem. Soc. 48, 517 (1956).

[31] H. Feilchenfeld, J. Phys. Chem. 61, 1133 (1957).

[32] G. R. Somayajulu, J. Chem Phys. 33, 1541 (1960); 34, (1961).

Table I

Heats of formation of some gaseous atoms from their reference states

Atom	$\Delta H_f(0^oK)$	$\Delta H_f(298.15^oK)$
H	51.62	52.09
C	170.00	171.30
N	112.55	113.00
O	58.98	59.55
S	66.13	66.42

equilibrium internuclear distance and dissociation energy in a sequence of similar diatoms with constant bond type are related by the expression:

$$k_e r_e / D_o = \text{const} \qquad (1)$$

The applicability of this relationship is limited to similar diatoms such as Cl_2, Br_2, I_2, etc., with same bond order and same type of bonds. However, for bonds of different type and of different order between two given atoms, we may use, as suggested by Fox and Martin[25], a relationship of the type deduced by Sutherland[33]. Expressing the potential energy of

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[33] G. B. B. M. Sutherland, Proc. Indian Acad. Sci. 8, 341 (1938); J. Chem. Phys. 8, 161 (1941).

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any diatom by means of the analytic function

$$U = ar^{-m} - br^{-n} \qquad (2)$$

and by differentiation and putting $(U')_{eq} = 0$ and $(U'')_{eq} = k_e$, it can be shown that

$$k_e r_e^2 / E = mn = \beta \qquad (3)$$

where a, b, m, n, and β are constants and E, the bond energy. It has been found that β is a constant for bonds of any type and of any order between two given atoms in their normal valence states. The validity

of Eq. (3) has now been illustrated for a few bonds. The results for a number of bonds have been presented in Table II. Some of them are based on estimated force constants and are not accurate.

OO Bonds

There is considerable controversy over the energy of the O-O bond of H_2O_2. Pauling[7] takes this to be equal to the difference in the heats of atomization of H_2O_2 and H_2O, which is 32.2 kcal. On the other hand, if we take this as equal to the difference in the heats of atomization of diethyl peroxide[34] and diethyl ether , E(O-O) = 48 kcal at 298.15° K.

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[34] R. E. Roberts and K. J. Laidler, J. Chem. Phys. 20, 574 (1952).

From Eq. (3) the energy of the O-O bond of H_2O_2 is 52 kcal. Both Skinner[26] and Walsh[28] have presented arguments to show that the OH bonds of H_2O_2 are not as strong as those of H_2O. If we take E(O-H) to be equal to the dissociation energy (101.3 kcal) of the OH radical, then from the heat of atomization (251.5 kcal) of H_2O_2, we obtain E(O-O) = 48.9 kcal. We consider a value around 50 kcal to be highly probable.

SS Bonds

From the heats of atomization[35] of the H_2S_n type molecules and from the heat of atomization[36] (503.88 kcal) of the gaseous S_8, a value around

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[35] F. Feher and G. Winkhaus, Z. anorg. u. allgem. Chem. 292, 210 (1957).

[36] G. B. Guthrie, D. W. Scott and G. Waddington, J. Am. Chem. Soc. 76, 1488(1954).

Table II

The force constants, bond lengths and bond energies of OO and NN type bonds[a]

Bond	Molecule	k_e	r_e	E	β
O=O	O_2	11.765	1.2074	117.95	0.1454
O-O	H_2O_2	3.5	1.47	52.0	
S=S	S_2	4.959	1.889	101.5	0.1744
S-S	H_2S_2	2.6	2.05	62.7	
Se=Se	Se_2	3.612	2.152	81.9	0.2043
Se-Se		1.91	2.34	51.2	
Te=Te	Te_2	2.37	2.59	71.5	0.2224
Te-Te		1.25	2.74	42.2	
N≡N	N_2	22.962	1.0976	225.1	0.1229
N=N		7.79[b]	1.25	99.0	
N-N	N_2H_4	3.7	1.47	65.0	
P≡P	P_2	5.556	1.8943	116.0	0.1718
P=P		3.704	2.0	86.2	
P-P		1.852	2.2	52.2	
As≡As	As_2	4.069	2.08	91.3	0.1928
As=As		2.712	2.22	69.3	
As-As		1.356	2.42	41.2	
Sb≡Sb	Sb_2	2.611	2.48	69.2	0.2321
Sb=Sb		1.74	2.62	51.5	
Sb-Sb		0.87	2.82	29.8	
Bi≡Bi	Bi_2	1.836	2.68	50.7	0.2599
Bi=Bi		1.224	2.82	37.5	
Bi-Bi		0.612	3.02	21.5	

(a) The k_e, r_e and E (D_e) values of the diatomic molecules are from footnote reference 32. The force constants of the O-O, S-S and N-N bonds are from footnote reference 37, and those of the other bonds are estimated (see footnote reference 12).

(b) Estimated value using bond energy of the N=N bond from azoisopropane.

63 kcal may be obtained for the energy of the S-S bond. On the basis of the β-value of S_2, and the force constant[37] and length of the S-S bond of

[37] E. B. Wilson, Jr., J. C. Decius and P. C. Cross, Molecular Vibrations (McGraw-Hill Book Company, Inc., New York, 1950), p. 175.

of H_2S_2, Eq. (3) gives 62.7 kcal for E(S-S). This is in good agreement with the observed value.

SeSe Bonds

The energy of the Se-Se bond may be deduced as shown below:

From footnote reference 32

$$Se_2(g) \longrightarrow 2Se(g) - 81.9 \text{ kcal}$$

From Stull and Sinke[38]

$$Se_6(g) \longrightarrow 3Se_2(g) - 65.4 \text{ kcal}$$

Whence $$Se_6(g) \longrightarrow 6Se(g) - 311.1 \text{ kcal}$$

and $$E(Se\text{-}Se) = 51.9 \text{ kcal/mole.}$$

[38] D. R. Stull and G. C. Sinke, Advances in Chemistry Series No.18, 1956.

The force constant of the Se-Se bond is not known; however, we have estimated[12] its value from the force constant of the SeH bond to be 1.91 md/A. Using this value, the energy of the Se-Se bond (as shown in Table II) is 51.2 kcal/mole in good agreement with the thermochemical value.

PP Bonds

From the k_e, r_e and D_o values of P_2, $\beta(PP) = 0.1718$. Assuming[12] the force constants of the single, double and triple bonds are in the ratio, 1:2:3, we have obtained the force constants of the single and double bonds from that of the triple bond. On the basis of Eq. (3) the energies of the P-P and P=P bonds are 52.2 and 86.2 kcal/mole respectively. The thermochemical value of E(P-P) from the heat of atomization of gaseous P_4 is 48 kcal/mole[39]. When corrected for strain, E(P-P) is 51 kcal/mole according

[39] F. S. Dainton, Trans. Faraday Soc. 43, 244 (1947).

to Dainton,[39] 51.3 kcal/mole according to Pauling and Simmonetta[40], and

[40] L. Pauling and M. Simmonetta, Proc. Nat'l. Acad. Sci. (Washington, D.C.) 20, 29 (1952).

54.5 kcal/mole according to Moffitt[41]. From the heat of atomization of

[41] W. E. Moffitt, Trans. Faraday Soc. 44, 987 (1948).

red phosphorus, the energy of the P-P bond according to Pitzer[17] is 53 kcal/mole. Our value for E(P-P) is 52.2 kcal/mole and is in good agreement with the values suggested by others.

AsAs Bonds

E(As-As) may be taken as one-sixth of the heat of atomization of gaseous As_4. Taking $D(As_2;g) = 91.3$ kcal/mole and $D(As_2\text{-}As_2) = 60.5$ kcal/mole,[33]

$\Delta H_A(As_4;g) = 243.1$ kcal/mole. Whence E(As-As) = 40.5 kcal/mole. Using Drowart and Goldfinger's[42] recent value of 70.8 kcal/mole for $D(As_2-As_2)$,

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[42] J. Drowart and P. Goldfinger, J. chim. phys. 55, 721 (1958).

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the value of E(As-As) = 42.2 kcal/mole. Our value for E(As-As) is 41.2 kcal/mole.

SbSb Bonds

Dainton[39] considers the value of E(Sb-Sb) to be lying in between 27 and 35 kcal/mole. Pauling[7] gives 30.2 kcal/mole. Our value using an approximate value for its force constant is 29.8 kcal/mole. Using the value of 62.4 kcal/mole for $D(Sb_2-Sb_2)$ and the value of 69.2 kcal/mole for $D(Sb_2)$, the heat of atomization of gaseous Sb_4 is 200.8 kcal/mole. This leads to 33.5 kcal/mole for E(Sb-Sb).

Thus the above results indicate the validity of Eq. (3). We will show the validity of Eq. (3) with respect to CC, CO, and NN bonds in subsequent sections.

Lack of reliable data on force constants of bonds in polyatomic molecules prevents us from making use of Eq. (3). Also there is a question about the definition of the force constant. As pointed out by Wilson, Decius and Cross[37], a force constant is defined only in terms of the complete potential function of which it is a member. As Szwarc and Evans[24] have pointed out, there does not seem to be any logical justification in using force constants derived from complicated potential functions. Strickly speaking, the force constants calculated on the basis of a simple valence force function are the correct

ones to use. However, in some cases, such as CO_2, where two force constants are obtained, one from the symmetric mode and another from the antisymmetric mode, a modification of the simple valence force function by way of introducing an interaction constant so as to give one force constant is necessary. In general, we would use force constants obtained on the basis of some sort of a modified valence force function. The energy values obtained thereby may not be very accurate but they would be far more superior to those obtained through speculative methods.

It is probably worthwhile to devote some space to include our comments on the validity of relationships of the form:

$$k_e r_e^{p+2} = \text{const.} \qquad (4)$$

and

$$E r_e^{p} = \text{const.} \qquad (5)$$

that follow from Eq. (3). Previously Fox and Martin[25] and very recently Feilchenfeld[26] have recommended the use of Eq. (5) for the derivation of the CC bond energies. For a number of reasons we do not consider Eqs. (4) and (5) to be reliable. For example, on the basis of the lengths of 1.337 A, 1.376 A and 1.397 A for the CC bonds of ethylene, cyanogen and benzene respectively, and on the basis of Eq. (5), one would expect the energy of the CC bond of cyanogen to be intermediate to the values for the CC bonds of ethylene and benzene. Similarly, one would expect the force constant of the CC bond of cyanogen to be intermediate to the force constants of the CC bonds of ethylene

and benzene. Unfortunately, the force constant of the CC bond of cyanogen is about 6.7 md/A, while the force constants of the CC bonds of ethylene and benzene are 9.6 and 7.6 md/A respectively[23]. If we use Eq. (5) for the prediction of the energy of the CC bond of cyanogen, we would end up with a value far higher than it should be. Similar considerations also invalidate the bond energies obtained by Dewar and Schmeising[13] using a relationship between bond length and bond energy. As expected, their value for the sp-sp CC bond is unusually high. Our value for the energy of this bond is 108 kcal while Dewar and Schmeising's value is 119.75 kcal.

From the foregoing discussion, it is quite clear that we are left with no other simpler alternative than to use Eq. (3) in the prediction of the energies of the CC bonds. However, given the energies of a few CC bonds such as >C-C<, >C=C< , and -C≡C-, we may estimate the energies of several other bonds in an unambiguous manner, without any recourse to Eq. (3). This has been shown in the following section.

4. METHODS OF ESTIMATION OF THE HEATS OF ATOMIZATION OF HOMOLOGOUS COMPOUNDS

It is customary to treat the heat of atomization of a molecule as the sum of contributions of atoms, groups of atoms, or bonds present in the molecule[43]. In the case of homologous compounds, the contributions of the

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[43] See G. J. Janz, Estimation of Thermodynamic Properties of Organic Compounds (Academic Press Inc., New York, 1958) for a summary of such methods.

groups may be obtained in a straightforward manner. However, no unambiguous values for the atoms or bonds have been found so far. This intricate situation has recently prompted Benson and Buss[44] to conclude that among the laws of

[44] S. W. Benson and J. H. Buss, J. Chem. Phys. 29, 546 (1958).

additivity, the law of additivity of atomic properties affords the zeroth order of approximation, the law of additivity of bond properties the first order of approximation, the law of additivity of group properties the second order of approximation, and so on. While we understand the circumstances that have led them to arrive at such a conclusion, we do not, however, agree with their conclusion. It can be shown that under equivalent assumptions, all the three methods of estimation would be equivalent and yield essentially the same result, whatsoever it may be. It is in this result we are interested. However, it should be pointed out that the results obtained through all these three methods may be made identical without necessarily making equivalent assumptions. The following discussion makes our points clear.

For example, the heats of atomization of n-alkanes may be estimated from the contributions of the methyl and methylene groups. The contribution of the methyl group may be taken as one-half of the heat of atomization of ethane. The contribution of the methylene group may be taken as equal to the constant increment in the heats of atomization of n-alkanes per CH_2 group. These group contributions may be conveniently split up into contributions for the primary and secondary carbon atoms, and hydrogen by assuming[45] the contribution

[45] The promotion energy of 1s to 2p of H is so high (10.2 ev) that it presumably makes s-p hybridization impossible for hydrogen.

of hydrogen to be equal to one-half of the dissociation energy of H_2. For simplicity we shall call the contribution of an atom, its valence state energy[46] (V). The heat of atomization of a molecule will then be given by

[46] A number of authors have discussed the valence states and the valence state energies of some atoms. For example, H. H. Voge, J. Chem. Phys. 16, 984 (1948) and J. H. Van Vleck, J. Chem. Phys. 1, 177, 219 (1933); 2, 20 (1934) have calculated that the tetrahedral valence state of carbon lies about 7 ev above the $s^2p^2\ {}^3P$ state. However, as C. A. Coulson, Valence (Clarendon Press, Oxford, England, 1952) has pointed out, the carbon atom of methane never gets into the valence state, and the energy needed to excite to the valence state never needs to be supplied to the system. We define the valence state energy as the energy actually supplied to the carbon atom in a molecule.

the sum of the valence state energies of all the atoms in it, i.e.,

$$\Delta H_A = \sum_{\text{(all atoms)}} V \qquad (6)$$

The n-alkanes may be also treated as consisting of one type[47] of

[47] Strictly speaking, three types of C-C bonds, viz., primary-primary, primary-secondary, and secondary-secondary C-C bonds have to be assumed, as has been suggested by V. M. Tateviski, Doklady Akad. Nauk, S.S.S.R. 75, 819 (1950). Unless one is interested in treating the isomeric paraffins, such an assumption need not be made.

$>C-C<$ bond as strong as that of diamond and two types of CH bonds, viz., primary and secondary CH bonds. Since the energy of the $>C-C<$ bond of diamond is known, the energies of the primary and secondary CH bonds may be obtained from the contributions of the methyl and methylene groups using the relationships

$$E(p\text{-}CH) = \frac{1}{3}\left[\Sigma\, V(CH_3) - \tfrac{1}{2}\, E(\,>C-C<\,)\right] \qquad (7)$$

and

$$E(s\text{-}CH) = \frac{1}{2}\left[\Sigma\, V(CH_2) - E(\,>C-C<\,)\right] \qquad (8)$$

Thus under these assumptions, which are all equivalent, the heats of atomization of n-alkanes may be estimated with an average deviation of $\pm$ 0.02 kcal/mole. There is, however, another method[48], which is as accurate

[48] G. E. Coates and L. E. Sutton, J. Chem. Soc. 1187 (1948).

as the above methods, but treats the primary and secondary CH bonds to be equal in strength. Then using the relationships (7) and (8), the energy of the $>C-C<$ bond may be estimated, but this value turns out to be much lower than it is in diamond. Both Mulliken and Coulson[49] have suggested that through

[49] C. A. Coulson, Quart. Rev. Chem. Soc. (London) 1, 144 (1947).

hyperconjugation, the $>C-C<$ bond of diamond is expected to be stronger and

shorter than the $>C-C<$ bond in the alkanes. The bond lengths do not seem to support their theory. Herzberg and Stoicheff[50] have shown that the length

[50] G. Herzberg and B. P. Stoicheff, Nature, 175, 79 (1955).

of the $>C-C<$ bond in a variety of compounds is constant and has the value of 1.543 ± 0.001 A. The length of the $>C-C<$ bond of diamond is also 1.544 A. Consequently, we are justified in treating these two bonds as equal in strength. Also the strength of the secondary CH bond compares favorably with that of such a bond in cyclohexane[51]. This shows that we are justified in treating the

[51] This is true at 298.15°K (see Table V.) but at 0°K, the strength of the CH bond in an open polymethylene chain is slightly greater than in cyclohexane. Dewar and Schmeising (see footnote reference 13) relate this difference at 0°K to the conformational effects. The all-trans conformation of a polymethylene chain is more stable than the all-gauche conformation of the cyclohexane; this makes the CH bonds of an open chain stronger than those of a closed chain. The conformational isomerism is probably not important at 298.15°K. The specific heat difference also may play some part in this.

strengths of the secondary and primary CH bonds as different.

Based on similar considerations, the general equation for the heat of atomization of a hydrocarbon may be written as

$$\Delta H_A = \sum_i n_i V_i + nV \qquad (9)$$

where V_i is the energy of the i-th type of carbon atom, and n_i, the number of such carbon atoms, n and V are the corresponding quantities for hydrogen. The valence state energies of a few distinct types of carbon atoms, viz., primary, secondary, tertiary, quaternary, trigonal and digonal carbon atoms have been recorded in Table III. The standards for the primary and secondary carbon atoms have been already explained. The valence state energy of the tertiary carbon atom has been obtained from the heats of atomization of 2-methyl alkanes. The valence state energy of the quaternary carbon atom has been taken to be equal to the heat of atomization of diamond. For simplicity we have assumed the carbon atoms of diamond, ethylene, and acetylene to be hybridized in the tetrahedral, trigonal and digonal states respectively.

Using bond energies, the heat of atomization of a hydrocarbon may be written as

$$\Delta H_A = \sum_i n_i E_i + \sum_j n_j E_j \qquad (10)$$

where E_i is the energy of the CC bond of the i-th kind, n_i, the number of such CC bonds, n_j and E_j are the corresponding quantities for the CH bonds. We have recorded in Table IV, the energies of 11 types of CC bonds and in Table V, the energies of 5 types of CH bonds. They are the >C-C< , ≥C-C≤ , ≡C-C≡ , >C-C≤ , >C-C≡ , ≥C-C≡ , >C=C< , >C=C= , =C=C= , -C≡C- and CC bond of benzene, and p-CH, s-CH, t-CH, ≥CH bonds, and ≡CH bonds. The energies of the >C=C< and -C≡C- bonds compatible with the energy of the >C-C< bond of diamond have been obtained on the basis of Eq. (3)[52]. With the help of the energies

[52] For consistency these values have been given up to the second place after the decimal, although such an accuracy is not warranted by the accuracy of the force constants.

Table III

Valence state energies of some typical carbon atoms

Type of carbon atom	Molecule	V(0°K)	V(298.15°K)
Primary	Ethane	178.26	181.42
Secondary	n-Alkanes	173.64	176.23
Tertiary	2-Methylalkanes	170.22	172.79
Quaternary	Diamond	169.40	170.86
Trigonal	Ethylene	162.74	165.05
Digonal	Acetylene	142.84	144.20

Table IV

The energies, lengths and force constants of some CC bonds

Bond	r_o	k_o	E (0^oK)	E (298.15^oK)
>C-C<	1.544	4.50	84.70	85.43
>C-C=	1.516	4.95	89.85	91.08
=C-C=	1.488	5.43	95.00	96.72
>C-C≡	1.460	5.73	96.35	97.33
=C-C≡	1.432	6.37	101.50	102.97
≡C-C≡	1.376	7.22	108.00	109.22
CC (C_6H_6)	1.397	7.69	118.50	119.64
>C=C<	1.337	9.60	135.50	136.66
>C=C=	1.312	10.24	139.16	140.43
=C=C=	1.288	10.87	142.33	144.20
-C≡C-	1.201	15.60	177.67	179.19

Table V

Bond energies of the CH bonds

Bond	Molecule	E (0^oK)	E (298.15^oK)
Primary CH	Ethane	96.92	98.32
Secondary CH	n-Alkanes	96.09	97.49
	Cyclohexane	95.94	97.48
Tertiary CH	2-Methylalkanes	94.80	96.73
=CH	Ethylene	99.12	100.45
≡CH	Acetylene	105.62	106.70

of these bonds, viz., >C-C< , >C=C< and -C≡C- bonds, and the valence state energies of the carbon atoms, the energies of the other CC bonds and CH bonds bonds have been obtained as shown below.

The valence state energy of the trigonal carbon atom from the heat of atomization of ethylene is 162.74 kcal/mole. The energy of the >C=C< bond of ethylene is 135.50 kcal/mole. If one-half of this amount (135.5 kcal/mole) is contributed by each trigonal carbon atom in ethylene for the formation of the double bond, then the remainder of the valence state energy of the trigonal carbon atom represents the strength of two sp^2 orbitals or the strength of one sp^2- sp^2 bond. Thus

$$E(>C-C<) = V(>C=) - \tfrac{1}{2} E(>C=C<) \qquad (11)$$

$$= 162.74 - \tfrac{1}{2}(135.50) = 94.99 \text{ kcal/mole.}$$

Similarly, the difference between the valence state energy of the digonal carbon atom and one-half of the energy of the -C≡C- bond, represents the strength of the sp orbital. Thus the strength of the sp orbital is 54 kcal/mole and the strength of the sp-sp bond is 108 kcal/mole.

The strengths of the remaining hybrid C-C bonds may be obtained by simple addition of the orbital strengths. Thus the energies of >C-C< , >C-C≡ and ≡C-C≡ bonds are 89.85, 96.35 and 101.50 kcal/mole respectively.

We may now estimate the energies of the >C=C= and =C=C= bonds. The energy of the =C=C= bond is obviously equal to the valence state energy of the digonal carbon atom. The energy of the >C=C= bond is equal to the arithmetic mean of the energies of the >C=C< and =C=C= bonds. Thus E(>C=C=) = 139.16 kcal/mole.

From the heat of atomization of ethylene and the energy of the >C=C< bond, we may obtain the energy of the ≥CH bond to be 99.12 kcal/mole. This value may also be obtained by the addition of the strengths of the trigonal orbital of carbon and the valence state energy of the hydrogen atom; thus E(≥CH) = 47.50 + 51.62 = 99.12 kcal/mole. Similarly, the energy of the ≡CH bond is equal to the sum of the strengths of the digonal orbital of carbon and the 1s orbital of hydrogen. Thus E(≡CH) = 54 + 51.62 = 105.62 kcal/mole.

Assuming both the ethylenic and benzenic CH bonds to be equal in strength, we obtain the strength of the CC bond of benzene from the heat of atomization of benzene to be 118.50 kcal/mole.

Bond energies which refer to 298.15°K have been also obtained by using the above procedures. They also have been presented in Tables IV and V.

We have also recorded in Table IV, the lengths and force constants of the CC bonds. The lengths of the C-C bonds are those obtained by additivity of the orbital radii[2]. The force constants are those which satisfy Eq.(5) and calculated by using the energies which refer to 0°K. The force constants for a few of these bonds are known and they compare satisfactorily with those calculated by us. For example, the force constant of the CC bond of benzene is known to be about 7.6 md/A. The value obtained by us is 7.69 md/A. Similarly, the force constant of the >C-C≡ bond of methyl acetylene is known to be 5.5 md/A and our value is 5.73 md/A. These results also prove the validity of Eq. (3).

It is also interesting to note that the strength of the hybrid orbital when plotted against the coefficient of mixing, λ, in the equation

$$\psi = \psi_s + \lambda \psi_p \qquad (12)$$

falls on a straight line as shown in Fig. 1. The values for the coefficient of mixing are those which satisfy the orthogonality condition

$$1 + \lambda^2 \cos \theta = 0 \qquad (13)$$

where θ is the angle between the axes of two equivalent orbitals. The values used for the strengths of the sp^3, sp^2 and sp orbitals are 42.35, 47.50 and 54 kcal/mole.

5. RESONANCE IN CLASSICAL AND NON-CLASSICAL MOLECULES

Molecules such as 1,3-butadiene, vinyl acetylene, etc. containing a C-C bond between two unsaturated carbon atoms are said to be conjugated; molecules such as propene, propyne, etc. containing a C-C bond between a saturated and an unsaturated carbon atom are said to be semiconjugated[13]. According to the π-electron theory, both conjugation and semiconjugation increase the stability of a molecule. Using either Eq. (9) or Eq. (10) we may estimate the expected heats of atomization of semiconjugated and conjugated hydrocarbons. If resonance were to be important, the observed heat of atomization must be higher than the expected value by an amount which we call the stabilization energy (SE). The results, which refer to 298.15° K, for a few typical molecules have been presented in Table VI and are now discussed.

Benzene

Benzene may be treated as consisting of 6 trigonal carbon atoms and

Table VI

Observed and calculated heats of atomization and the stabilization energies of some unsaturated hydrocarbons. ($T = 298.15^{o}K$)

Compound (gas)	ΔH_A(Obs.)	ΔH_A(Calc.)[c]	SE
Benzene	1320.52	1302.84	17.68
Toluene	1603.87	1588.44	15.43
p-Xylene	1887.01	1874.04	12.97
Mesitylene	2170.62	2159.64	10.98
n-Butylbenzene	2445.56	2429.67	15.89
n-Decylbenzene	4128.00	4112.13	15.87
Diphenyl	2535.30[a]	2501.50	33.80
Diphenylbutadiene	3406.8 ± 1.8[b]	3370.16	36.7 ± 1.8
Styrene	1751.90	1737.12	14.78
Phenylacetylene	1607.14[b]	1591.24	15.90
Propene	821.56	824.06	- 2.50
1-Pentene	1382.40	1384.88	- 2.44
1-Decene	2784.47	2786.93	- 2.46
Isobutene	1105.26	1109.66	- 4.40
trans-2-Butene	1104.33	1109.66	- 5.33
cis-2-Butene	1103.28	1109.66	- 6.38
1,4-Pentadiene	1248.02	1253.15	- 5.13
Trimethylethylene	1387.57	1395.26	- 7.69
Tetramethylethylene	1668.79	1680.86	-12.07
Methylacetylene	677.94	678.18	- 0.24
Dimethylacetylene	959.25	963.78	- 4.53
1,3-Butadiene	971.41	972.74	- 1.33
Allene	676.34	682.66	- 6.32

(a) See footnote reference 53.

(b) See footnote reference 48.

(c) Calculated on the basis of Eq. (9).

6 hydrogen atoms. On the basis of Eq. (9), the expected heat of atomization of benzene is 1302.84 kcal/mole, while its observed value is 1320.52 kcal/mole. They lead to a value of 17.68 kcal/mole for the stabilization energy of benzene. The stabilization energy of benzene may also be estimated in a number of other ways. Since all our calculations of the valence state energies and bond energies are based on the fundamental assumption that the valence state of hydrogen is invariant from molecule to molecule, the stabilization energy of benzene may be simply obtained from the heats of formation of ethylene and benzene as shown below:

$$\begin{aligned} SE(\text{Benzene}) &= 3\,\Delta H_f(\text{Ethylene}) - \Delta H_f(\text{benzene}) \\ &= 3(12.50) - 19.82 = 17.68 \text{ kcal/mole.} \end{aligned}$$

According to Dewar and Schmeising, the stabilization energy of benzene is given by:

$$SE = SR - HE \tag{14}$$

where SR (spurious resonance energy), which represents the difference in the heats of hydrogenation of one molecule of benzene and three molecules of ethylene, is

$$\begin{aligned} SR &= \Delta H_h\,(\text{benzene}) - 3\,\Delta H_h\,(\text{ethylene}) \\ &= -49.25 - 3(-32.74) = 48.97 \text{ kcal/mole;} \end{aligned}$$

and HE, which represents the effect of different hybridization of the

carbon atoms in the unsaturated and saturated hydrocarbons and also the effect of different strengths of the primary and secondary CH bonds in the end products, is given by:

$$HE = 3\left[E(\geq C\text{-}C\leq) - E(>C\text{-}C<)\right] - 6\left[E(\geq CH) - E(CH, \text{ethane})\right]$$

$$+ \; 12\left[E(CH, \text{ethane}) - E(CH, \text{cyclohexane})\right]$$

$$= 3(96.72 - 85.43) - 6(100.45 - 98.32) + 12(98.32 - 97.48)$$

$$= 31.17 \text{ kcal/mole.}$$

Whence SE(Benzene) = 48.97 - 31.17 = 17.80 kcal/mole.

However, as pointed out by Dewar and Schmeising[13], part of this energy must represent the σ-bond relief strain energy (SRE). It may be noted, that in benzene there is only one electron available for each π-bond, while in ethylene there are two. A two-electron π-bond compresses the σ-bond more than a one-electron π-bond does. Thus there is some relief of strain in benzene, which is seen to increase the valence state energy of each trigonal carbon atom of benzene by 2.95 kcal. But how much of this stabilization energy represents the strain relief energy is yet to be found out.

Toluene: $C_6H_5\text{-}CH_3$

Assuming that toluene consists of 6 trigonal carbon atoms, one primary carbon atom and 8 hydrogen atoms, we have estimated its heat of atomization to be 1588.44 kcal/mole. Its observed heat of atomization is 1603.87 kcal/mole; whence its stabilization energy is 15.43 kcal. If hyperconjugation were to be

important in toluene, it should have greater stabilization energy than benzene. However, replacement of hydrogen by methyl group lowers the stabilization energy of benzene by 2.25 kcal.

We have presented in Table VI the stabilization energies of p-xylene and mesitylene. They show that the lowering of the stabilization energy of benzene increases with the number of hydrogen atoms replaced by the methyl groups. The higher alkyl substituted benzenes have a somewhat higher stabilization energy than toluene. From n-butylbenzene onwards, the stabilization energy is constant, being equal to 15.87 ± 0.02 kcal.

Diphenyl: C_6H_5-C_6H_5

Diphenyl may be treated as consisting of 12 trigonal carbon atoms and 10 hydrogen atoms. Thus its heat of atomization is 2501.5 kcal/mole, while its observed value[53] is 2535.30 kcal/mole. Because of the presence

[53] See J. S. Roberts and H. A. Skinner, Trans. Faraday Soc. 45, 339 (1949).

of a C-C bond between the two rings, its stabilization energy is expected to be greater than twice the stabilization energy of benzene (35.36 kcal). The value found is only 33.80 kcal, indicating a slight decrease in the stabilization energy.

Propene: CH_2=CH-CH_3

Treating propene as consisting of two trigonal carbon atoms, one primary carbon atom and 6 hydrogen atoms, we have estimated its stabilization

energy to be -2.50 kcal. Since the ethylenic carbon atoms are taken as standard for the trigonal carbon atom, the stabilization energy of ethylene is zero. The negative stabilization energy of propene, therefore, shows that methylation lowers the stabilization energy of ethylene. The stabilization energies of trans-2-butene, trimethylethylene and tetramethylethylene, presented in Table VI, show that the lowering of the stabilization energy of ethylene increases with the number of hydrogen atoms replaced. These results are fully consistent with our results for benzene and its methyl derivatives. It is also interesting to note that among the disubstituted ethylenes, cis-2-butene has the lowest stabilization energy (-6.38 kcal) followed by trans-2-butene (-5.33 kcal) and isobutene (-4.40 kcal).

The lowering in the stabilization energy of ethylene is constant (2.46 $\pm$ 0.02 kcal) from 1-pentene to 1-eicosene.

Propyne: $HC{\equiv}C{-}CH_3$

Treating propyne as consisting of two digonal carbon atoms, one primary carbon atom and 4 hydrogen atoms, we have estimated its stabilization energy to be -0.24 kcal. This indicates that methylation slightly lowers the stabilization energy of acetylene. This lowering is not much when one hydrogen atom is replaced but when both the hydrogen atoms are replaced as in dimethyl acetylene, there is considerable lowering in the stabilization energy of acetylene.

1,3-Butadiene: $CH_2{=}CH{-}CH{=}CH_2$

We may treat this molecule as consisting of 4 trigonal carbon atoms

and 6 hydrogen atoms. On the basis of Eq. (9), its heat of atomization is 972.74 kcal/mole while its observed value is 971.41 kcal/mole. This shows that the stabilization energy of 1,3-butadiene is -1.33 kcal. This being negative, we may conclude that π-electron resonance is unimportant in the ground state of this molecule.

Styrene: $C_6H_5-CH=CH_2$

Treating styrene as consisting of 8 trigonal carbon atoms and 8 hydrogen atoms, we have found its stabilization energy to be 14.76 kcal. This is less than that for benzene and shows that replacement of hydrogen atom even by vinyl group has the same effect as replacement of hydrogen atom by methyl.

Diphenylbutadiene: $C_6H_5-CH=CH-CH=CH-C_6H_5$

Coates and Sutton[48] have determined the heat of atomization of diphenylbutadiene to be 3406.8 ± 1.8 kcal at 293°K. Treating this molecule as consisting of 16 trigonal carbon atoms and 14 hydrogen atoms, we have estimated its heat of atomization to be 3370.1 kcal/mole. This leads to a value which is approximately equal to twice the stabilization energy of benzene. Consequently, we may conclude that there is no resonance in addition to that already present in the two benzene rings.

Phenylacetylene: $C_6H_5-C\equiv CH$

The stabilization energy of this molecule has been found to be about

15.90 kcal; this is also less than that for benzene.

Allene: $CH_2{=}C{=}CH_2$

Assuming that this molecule consists of two trigonal and one digonal carbon atoms, and 4 hydrogen atoms, we have calculated its heat of atomization to be 682.66 kcal/mole. Its observed value is 676.34 kcal/mole leading to a stabilization energy of -6.32 kcal. Although the central carbon atom of allene is presumably hybridized in the digonal state, it is not bonded in the same way as the digonal carbon atom of acetylene. Consequently, the central carbon atom of allene may have a different valence state energy, 137.88 kcal/mole. This value may be useful in the calculation of the heats of atomization of molecules containing the $=C=$ atoms. Thus we may estimate the heat of atomization of butatriene ($CH_2{=}C{=}C{=}CH_2$) to be 814.22 kcal/mole.

Thus the results presented above provide no evidence in favor of π-electron resonance in the ground states of classical molecules. In the case of the non-classical benzene molecule, much of the stabilization is due to the relief of the σ-bond strain. Alkylation has been found to lower the stabilization energies of ethylene, benzene and acetylene. It is also known[54] that alkylation considerably lowers the ionization potentials of

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[54] W. C. Price, Chem. Revs. 41, 257 (1947).

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unsaturated and aromatic hydrocarbons. We feel that there should be some relationship between the lowering of the ionization potential and the

lowering of the stabilization energy upon alkylation. For example, the ionization potential of propene is 0.8 ev lower than that of ethylene and the difference in the stabilization energies of ethylene and propene is 2.50 kcal. The ionization potential of methylacetylene, on the other hand, is just 0.11 ev lower than that of acetylene; similarly we find the lowering in the stabilization energy of acetylene by one methyl group is 0.24 kcal only. The ionization potentials of these compounds have been discussed by a number of authors[6,54-56]. Walsh[56] has pointed out that

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[55] J. Fain and A. L. Matsen, J. Chem. Phys. 26, 376 (1957).

[56] A. D. Walsh, Ann. Rep. Chem. Soc. (London) 44, 33 (1947).

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the replacement of hydrogen in ethylene by methyl group weakens the σ-bond in C=C with the consequence that the π-electron is more easily removed. Mulliken[6] ascribes this difference largely to stabilization of the positive ion, $C_3H_6^+$ in consequence of methylation.

If alkylation lowers the stabilization energies of ethylene, acetylene and benzene, it should also lower the strengths of some bonds present in those molecules. It is, however, difficult to say which particular bond is affected by alkylation. In propene, the chances are that the >C=C< bond may not be as strong as in ethylene. It is also possible that the >C-C< bond may not be as strong as indicated by the strengths of the sp^2 and sp^3 orbitals of carbon. As noted in the introduction, an sp^2 - sp^3 bond does not appear to be stronger than indicated by the strengths of the sp^2 and sp^3 orbitals.

6. RESONANCE IN HOMOLOGOUS COMPOUNDS CONTAINING NON-HYDROCARBON GROUPS

In this Section we have estimated the stabilization energies of compounds containing non-hydrocarbon groups such as -CHO, -COOH, >C=O, etc. The heats of atomization of these compounds have been estimated on the basis of the contributions of the groups (ZV values) which are presented in Table VII. These values have been obtained from the heats of atomization of such simple molecules as formaldehyde, formic acid, etc., by subtracting the contribution of the hydrogen atoms.

Making certain simple assumptions we have also estimated the energies of the bonds in these molecules. These results are now discussed. All the energies quoted in the following discussion refer to 298.15°K.

n-Alcohols

The increment in the heat of atomization per methylene group in several homologous compounds containing no non-hydrocarbon groups is fairly constant being equal to 280.41 kcal. However, the presence of a non-hydrocarbon group in a hydrocarbon seems to influence the strengths of CC and CH bonds. Rossini[57]

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[57] F. D. Rossini, J. Research, N.B.S. (U.S.) 13, 189 (1934).

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has found that the increment per CH_2 is slightly higher in n-alcohols than in paraffins. We have found this difference to be about 0.62 kcal per CH_2 group; this would appear as the stabilization energy if the heats of formation of n-alcohols were to be treated on the basis of the value for the methylene group of the paraffins.

Table VII

Contributions of some groups to the heats of atomization

(ΣV values in kcal/mole)

Group	Molecule	$\Sigma V(0^{o}K)$	$\Sigma V(298.15^{o}K)$
$-CH_3$	Ethane[a]	333.12	337.69
$>CH_2$	n-Alkanes[a]	276.88	280.41
$>CH$	Paraffins[a]	221.84	224.81
$-\overset{\mid}{\underset{\mid}{C}}-$	Diamond[a]	169.40	170.86
$-CH=CH_2$	Ethylene[a]	480.34	486.37
$-C\equiv CH$	Acetylene[a]	337.29	340.50
$-C_6H_5$	Benzene[b]	1254.10	1268.43
-O-	Ethers	100.52	101.69
-OH	Alcohols	152.14	153.78
-S-	Thioalkanes	55.00	55.44
-SH	Thiols	114.61	115.43
$>C=O$	Formaldehyde	255.78	258.57
-CHO	Formaldehyde	307.40	310.66
-COOH	Formic acid	428.23	432.88
$-CONH_2$	Formamide		497.03
-COSH	Thiolacetic acid		(381.90)
-CN	Nitriles	255.39	257.20

(a) The ΣV values for these compounds are based on the valence state energies of the carbon atoms given in Table III.

(b) The values include the stabilization energy of benzene. The stabilization energy of benzene is 19.56 kcal at $0^{o}K$ and 17.68 kcal at $298.15^{o}K$.

We have found that the heats of atomization of n-alcohols can be satisfactorily estimated on the basis of the ΣV values: 337.69 kcal for the CH_3, 281.03 kcal for the CH_2 and 153.78 kcal for the OH group. These results have been presented in Table VIII. The calculated values agree excellently with the observed values from n-hexanol to n-decanol. In the case of methanol, the calculated value is 4.27 kcal higher than the observed value. The calculated values are slightly higher than the observed values for the other alcohols up to n-pentanol.

From the ΣV value of the OH group, the valence state energy of the oxygen atom is 101.7 kcal/mole. This value is quite close to the valence state energy of the oxygen atom in diamyl ether. In diamyl ether it represents the sum of the strengths of two equivalent orbitals of oxygen (which are probably tetrahedral). On this basis the strength of the oxygen orbital is 50.85 kcal and the strength of the >C-O bond by the addition of the orbital strengths, is 93.6 kcal. If we assume that the oxygen orbitals are also equivalent in alcohols, then the energies of the >C-O and O-H bonds would be 93.6 kcal and 102.9 kcal respectively. The bond energies which refer to $0^{o}K$ for the >C-O and O-H bonds are 92.6 and 101.9 kcal respectively.

Aldehydes, Ketones and Acids

From the heats of atomization of formaldehyde and formic acid, the ΣV values of >C=O, -CHO, and -COOH groups have been found to be 258.57, 310.66 and 432.88 kcal respectively. On the basis of these values, we have estimated the stabilization energies of some compounds containing these groups and presented them in Table IX. These results are now discussed.

Table VIII

Comparison of the observed and estimated heats of atomization of n-alcohols ($T = 298.15^{o}K$)

Compound (gas)	ΔH_A (Obs.)[a]	ΔH_A (Calc.)[b]	Deviation
Methanol	487.20	491.47	- 4.27
Ethanol	771.32	772.50	- 1.18
n-Propanol	1052.93	1053.53	- 0.60
n-Butanol	1334.26	1334.56	- 0.30
n-Pentanol	1615.34	1615.59	- 0.25
n-Hexanol	1896.62	1896.62	0
n-Heptanol	2177.65	2177.65	0
n-Octanol	2458.68	2458.68	0
n-Nonanol	2739.71	2739.71	0
n-Decanol	3020.74	3020.74	0

(a) Taken from footnote reference 57.

(b) Estimated on the basis of the ΣV values; 337.69 kcal for CH_3, 281.03 kcal for CH_2, and 153.78 kcal for OH.

Table IX

Comparison of the observed and estimated heats of atomization of some compounds containing >CO, -CHO and -COOH groups. ($T = 298.15^{o}K$)

Compound (gas)	ΔH_A(Obs.)	ΔH_A(Calc.)	SE
Formaldehyde	362.75	362.75	0
Acetaldehyde	650.18	648.35	1.87
n-Propionaldehyde	932.00[a]	928.76	3.24
n-Butyraldehyde	1214.00[a]	1209.17	4.83
Vinylaldehyde	801.81[a]	797.03	4.78
Allylaldehyde	1077.90[a]	1077.44	0.46
Benzaldehyde	1582.40[a]	1561.40	21.00
α-Ketopropionaldehyde	907.20[a]	906.92	0.28
Acetone	937.71	933.95	3.76
Methyl ethyl ketone	1219.64[a]	1214.36	5.28
Formic Acid	484.97	484.97	0
Acetic acid	774.59	770.57	4.02

(a) Taken from footnote reference 53.

Comparison of the stabilization energies of acetone show that methylation increases the stabilization energy of formaldehyde (which is zero because it is taken as the standard) by 1.9 kcal per methyl group. For each methylene group introduced into acetaldehyde and acetone the stabilization energy appears to increase by 1.5 kcal. This shows that we may treat the heats of atomization of aldehydes and ketones by using somewhat higher ΣV values for the methyl and methylene groups.

Vinylaldehyde and benzaldehyde have higher stabilization energies than their parent compounds ethylene and benzene. This shows that conjugation stabilizes these molecules. On the other hand, allylaldehyde and α-ketopropionaldehyde (CH_2COCHO) have very small stabilization energies.

Acetic acid has a high stabilization energy of 4 kcal.

The heats of formation of some of the above compounds are not accurately known; this prevents us from making any assertions about the effects of conjugation and semiconjugation in these compounds.

Bond energies in formic acid and formaldehyde may be obtained as follows: Assuming that the CH bonds in formaldehyde are as strong as those in ethylene, we have estimated the energy of the >C=O bond to be 161.9 kcal. If we assume that the doubly-bound oxygen atoms and carbon atoms in both formaldehyde and formic acid are identical, then the difference in the ΣV values of the -COOH and -CHO groups represents the valence state energy of the singly-bound oxygen atom. Thus we obtain 122.2 kcal. Assuming that this value represents the sum of the strengths of two equivalent orbitals of oxygen (which are probably trigonal), the strength of each orbital of oxygen is 61.1 kcal. By the addition of the

orbital strengths, the energies of the ≥C-O and O-H bonds are 109.5 and 113.2 kcal respectively.

Bond energies which refer to $0^{o}K$ of the >C=O, ≥C-O and O-H bonds are 160.8, 107.9 and 112.0 kcal respectively.

In the derivation of these bond energies, we have made a number of assumptions which probably need some justification. For this we show that the energies of the CO bonds deduced by us lead to force constants which compare satisfactorily with their literature values. This has been shown in Table X. The β-constant for the CO bonds has been obtained using the k_o, r_o and E values of the =C=O bond of CO_2. In this calculation bond energies which refer to $0^{o}K$ have been used. On the basis of Eq. (3), we have calculated the force constants of the >C-O, ≥C-O and >C=O bonds to be 5.0, 6.3 and 12.0 md/A respectively, in good agreement with the literature values[23] of 5.0, 6.4 and 12.1 md/A respectively.

Thiols and Thiaalkanes

The available data on the heats of atomization of some thiaalkanes and thiols do not seem to indicate any stabilization of the methylene and methyl groups in these compounds. Their heats of atomization have been estimated on the basis of 55.44 kcal for the -S- and 115.43 kcal for the -SH groups. They are compared with the experimental values in Table XI. The calculated values are seen to be quite satisfactory.

From the valence state energy of the sulphur atom in thiaalkanes, the strength of the sulphur orbital has been found to be 27.7 kcal. This leads to 70.4 kcal for the energy of the >C-S bond.

Table X

The force constants, lengths and energies of CO bonds (β = 0.1092)

Bond	Molecule	E ($0^{o}K$)	r_o	k_o(Calc.)	k_o(Lit.)[a]	E($298.15^{o}K$)
>C-O-	CH_3CH	92.6	1.423[b]	5.0	5.0	93.6
≥C-O-	HCOOH	107.9	1.367[b]	6.3	6.4	109.5
>C=O	HCHO	160.8	1.21	12.0	12.1	161.9
=C=O	CO_2	191.0	1.16	15.5[c]	15.5	192.2

(a) Collected from footnote reference 23.

(b) Taken from footnote reference 2.

(c) The literature value has been assumed to obtain the β-constant for the CO bonds.

Table XI

Comparison of the observed and calculated heats of atomization of some thiaalkanes and alkanethiols. (298.15°K)

Compound (gas)	ΔH_A(Obs.)	ΔH_A(Calc.)[c]	Deviation
2-Thiapropane	730.54[a]	730.82	- 0.28
2-Thiabutane	1011.11[a]	1011.23	- 0.12
2-Thiapentane	1291.88[a]	1291.64	0.24
3-Thiapentane	1292.29[a]	1291.64	0.65
5-Thianonane	2414.74[b]	2413.28	1.46
Thiacyclopentane	1176.44[b]	1177.08	0.64
Thiacyclohexane	1458.96[b]	1457.39	1.57
Methanethiol	449.78	453.12	- 3.34
Ethanethiol	732.60[a]	733.53	- 0.97
1-Propanethiol	1013.08[a]	1013.94	- 0.86
1-Butanethiol	1293.39[a]	1294.35	- 0.96
1-Pentanethiol	1574.70[a]	1574.76	- 0.06

(a) D. W. Scott, G. B. Guthrie, J. P. McCollough and G. Waddington, J. Chem. Eng. Data, 4, 246 (1959).

(b) S. Sunner, Acta Chem. Scand. 9, 837 (1955).

(c) Calculated on the basis of the ΣV values given in Table VII.

From the EV value of the -SH group, the valence state energy of the sulphur atom in thiols has been found to be 63.44 kcal. A value close to this has been also found in a number of compounds, viz., H_2S_2, S_8, CS_2, thiophene, etc. In thiols this value is sufficient to form one >C-S bond as strong as that of thioalkanes and one S-H bond as strong as that (87.7 kcal) of H_2S.

In thiolacetic acid, sulphur is supposed to be in the trigonal state of hybridization. From the heat of atomization[58] of this compound, the

[58] S. Sunner, Acta Chem. Scandinavica 9, 837 (1955).

valence state energy of the sulphur atom has been found to be 71.24 kcal, a value which may be obtained also from the heat of atomization of H_2S. Assuming equivalent orbitals, we obtain 84.0 kcal for the energy of the >C-S bond and 87.7 kcal for the energy of the S-H bond in thiolacetic acid.

From the heat of atomization of CS_2, the energy of the =C=S bond is 135.4 kcal.

Nitriles

The normal contribution of the -CN group may be taken as equal to the sum of the valence state energies of the digonal carbon atom and the triply-bound nitrogen atom of N_2. Thus EV(CN) = 257.2 kcal. By subtracting the strength of one digonal orbital of carbon from this, we obtain E(-C≡N) to be 202.6 kcal. On the basis of the group contributions, we have estimated the heats of atomization of a few nitriles and compared them with the experimental values in Table XII. Also assuming all other bonds to be normal, we have

Table XII

Comparison of the observed and calculated heats of atomization of some nitriles, and the energies of the -C≡N bonds in these compounds (298.15°K)

Compound (gas)	ΔH_A(Obs.)	ΔH_A(Calc.)	E(-C≡N)[b]
Benzonitrile	1524.55[a]	1525.63	201.51
α-Toluinitrile	1805.03[a]	1806.04	201.58
Acrylonitrile	739.47[a]	743.57	198.49
Acetonitrile	590.87	594.89	198.57
Hydrogen cyanide	303.86	309.29	197.16
Cyanogen	494.10	514.40	192.44

(a) Taken from footnote reference 53.

(b) Calculated under the assumption that all other bonds in these molecules are normal.

estimated the energies of the -C≡N bonds in these molecules and presented them in the same Table. It can be seen that in benzonitrile and α-tolunitrile, the -C≡N bonds have nearly the normal energies. In acrylonitrile, acetonitrile and hydrogen cyanide, the energy of the -C≡N bond is ~198 kcal. Its value (192.4 kcal) is considerably lower in cyanogen. These results show that resonance is not important in nitriles.

Amides

From the heat of atomization of formamide, we have estimated the EV value of the $-CONH_2$ group to be 497.0 kcal. On the basis of group contributions, the heat of atomization of acetamide is 834.7 kcal. Its observed value[53] is 836.5 kcal showing that it has a stabilization energy of 1.8 kcal.

Structural data[59] for formaldehyde indicate that its nitrogen atom is

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[59] R. J. Kurland and E. B. Wilson, Jr., J. Chem. Phys. 27, 585 (1957).

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hybridized in the trigonal state. The valence state energy of this nitrogen atom is 134.4 kcal. This may be compared with the value 124.0 kcal for the valence state energy of the nitrogen atom of ammonia; this is probably in the tetrahedral state of hybridization. The strength of the trigonal orbital of nitrogen is 44.8 kcal. By the additivity of orbital strengths, the energy of the trigonal-trigonal carbon-nitrogen bond is 93.2 kcal and that of $N(sp^2)$-H bond is 96.9 kcal. The energy of the N-H bond of ammonia is only 93.44 kcal.

Amines and other compounds of nitrogen

From the valence state energy of the tertiary nitrogen atom, the strength of the bonding orbital of nitrogen with that of carbon has been found to be ~32.8 kcal. This leads to the values: 75.0, 80.6, and 86.9 kcal for the energies of the >C-N, ≥C-N and ≡C-N bonds. On the basis of these values, we have estimated the energies of the N-H bonds in a number of amines. They are as follows: methylamine 90.7 kcal, ethylamine 90.9, n-propylamine 91.0, n-butylamine 91.3, n-hexylamine 94.7, n-heptylamine 94.9, cyanoamine ($CN-NH_2$) 92.2, aniline 93.9, benzylamine 94.5, allylamine 94.1, dimethylamine 84.9, and diethylamine 86.2 kcal. These show that N-H bonds in aniline, benzylamine, cyanoamine, n-hexylamine, etc., are nearly as strong as those of ammonia, while they are slightly weaker in lower primary amines. In secondary amines E(N-H) is only 86 kcal.

Assuming the energy of the >C-N bond to be 75 kcal, the energy of the >C=N- bond in n-butylisobutylideneamine, $CH_3(CH_2)_3-N=CH-CH(CH_3)_2$ is ~136 kcal. On the basis that E(≥C-N) = 81.6 kcal, the energy of the >C=N- bond in benzylideneanil, $C_6H_5-CH=N-C_6H_5$ is also ~136 kcal. However, from dibenzylidene ethylenediamine $C_6H_5-CH=N-CH_2-CH_2-N=CH-C_6H_5$, the energy of the >C=N- bond is only 126 kcal. In both dibenzylidene ethylenediamine and dibenzylideneazine, $C_6H_5-CH=N-N=CH-C_6H_5$, the valence state energy of the nitrogen atom is ~ 90 kcal. Consequently, if we assume the energy of the >C=N- bond in dibenzylideneazine to be 126 kcal, the energy of the N-N bond would be 64.5 kcal. From Eq. (3), the energy of the N-N bond in hydrazine is 65 kcal. For E(N-N), Walsh[28] gives 65 kcal, but Pauling[7] gives only 38.4 kcal. We recommend the value 65 kcal.

Assuming that E(>C-N) = 75 kcal, the energy of the N=N bond in azoisopropane is 99 kcal.

The heats of formation of these compounds are from Coates and Sutton[48] and from Roberts and Skinner[53].

7. CONCLUSION

It has been shown that alkylation lowers the stabilization energies of ethylene, benzene and acetylene. Also it has been shown that the lowering increases with the number of hydrogens replaced in ethylene, benzene and acetylene. Also the fact that in these compounds the increment per methylene group is normal, being equal to that in n-alkanes suggests that it is the unsaturated part, not the alkyl chain, that has lost the energy. These results need explanation.

The results for aldehydes, ketones, acids, etc., indicate considerable strengthening of the bonds in the alkyl chain. This strengthening has been found to be maximum in acids, followed by aldehydes, amides, alcohols, etc. Groups such as $-NH_2$, -SH, >N, -O-, -S-, etc., do not seem to have much effect on the strengths of the bonds in the alkyl chain. The cyano group has no such effect. Although we may estimate the heats of atomization of acids, aldehydes, ketones, alcohols, etc., by adopting somewhat higher EV values for the CH_2 and CH_3 groups, we still need to explain the reason for this.

The stabilization energy of benzaldehyde has been found to be greater than that of benzene. Similarly, the stabilization energy of vinylaldehyde is greater than that of ethylene. If conjugation is not the factor, a suitable explanation for stabilization in these compounds is desirable.

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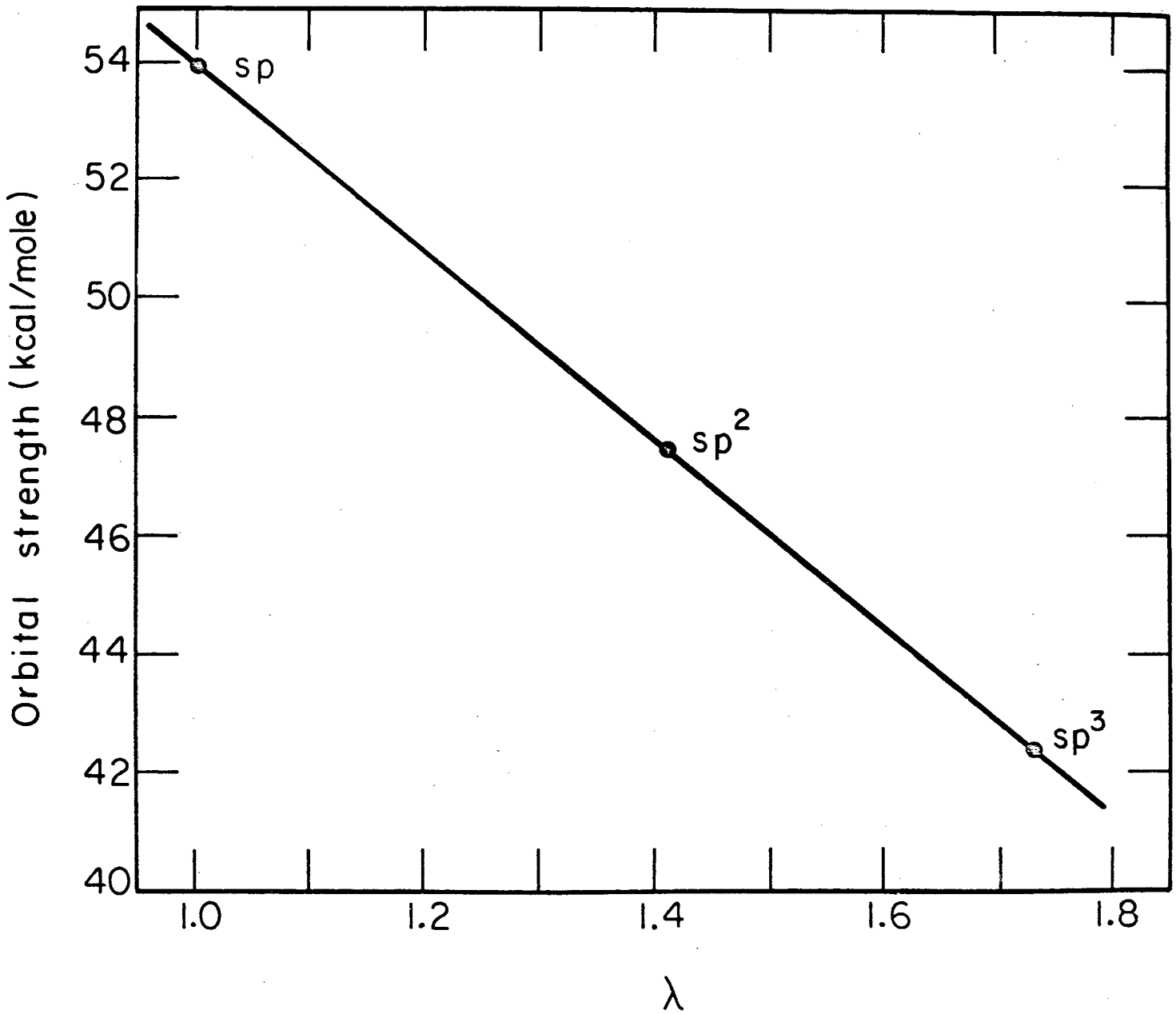

Fig. 1. Orbital strength as a function of the coefficient of mixing (λ) for the s-p hybrid orbitals of carbon.