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Abstract

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ON THE DEPENDENCE BETWEEN THE σ-ELECTRON CHARGES OF BONDS AND THE ENERGY CHARACTERISTICS OF SATURATED HYDROCARBONS

(Presented by Academician V. N. Kondrat' ev, July 2, 1963)

Numerous works have been devoted to calculations of the electronic charges of atoms and bonds by methods of quantum chemistry. Recently such calculations have been applied to the distribution not only of π-, but also of σ-electrons (^{1}). The calculated electronic charges are then compared with various properties of molecules and of their structural elements, but not with the energies of σ-bonds.

The author (see the reviews (^{2}, ^{3})) has developed methods for determining the π- and σ-electronic charges of bonds on the basis of quantitative data on the properties of molecules and their structural components; it was shown that: 1) the electronic charges of bonds may be regarded as a fundamental characteristic of covalent bonds in organic compounds; 2) by operating with numerical values of the electronic charges of bonds, one can construct simple schemes for calculating practically and theoretically important characteristics of individual bonds and entire molecules; and 3) to a first approximation, the dependence between the charges and properties of bonds may be taken as linear. However, in establishing the relation between the σ-electronic charges and bond energies, the author made certain simplifying assumptions that were not entirely justified, which was partly reflected in the interpretation of the calculation results. It is therefore expedient to consider the possibility of a more rigorous application of the linear dependence for deriving relations between the σ-electronic charges of bonds and the heats of formation of saturated hydrocarbons (the same method can also be applied to their saturated derivatives), first, and the thermochemical bond energies, second.

In what follows the following notation is used: $H^{\text{at}}_{C_{nH}m}$ is the heat of atomization of one mole of the hydrocarbon $C_{nH}m$ under standard conditions, numerically equal and opposite in sign to the heat of its formation from atoms; $H^{\text{el}}_{C_{nH}m}$ is the heat of "elementization" of one mole of the hydrocarbon $C_{nH}m$, numerically equal and opposite in sign to the heat of formation of one mole of it under the same conditions from the elements; L_C is the heat of atomization (sublimation) of diamond; H^{at}_H is the heat of atomization of hydrogen (equal to 52.089 kcal/g-atom); Q_{CC} and Q_{CH} are the thermochemical energies of the σ-bonds CC and CH; A_{CC} and A_{CH} are the σ-electronic charges of the same bonds; a_{CC}, a_{CH}, b_{CC}, b_{CH}, and q are constants to be discussed below.

In a saturated hydrocarbon $C_{nH}m$ there are m CH bonds and $(4n-m)/2$ CC bonds. According to the well-known relation between heats of formation and thermochemical bond energies,

$$\sum^{\frac{4n-m}{2}} Q_{CC} + \sum^{m} Q_{CH} = H^{\text{at}}_{C_{nH}m}. \tag{1}$$

The linear dependence between the σ-electronic charges and the energies of bonds is expressed in the form

$$\begin{aligned} Q_{CC} &= a_{CC}A_{CC} + b_{CC}, \\ Q_{CH} &= a_{CH}A_{CH} + b_{CH}. \end{aligned} \tag{2}$$

As is known,

$$H^{\text{at}}_{C_{nH}m} = H^{\text{el}}_{C_{nH}m} + nL_C + mH^{\text{at}}_H. \tag{3}$$

One might suppose that the heat of sublimation of diamond is equal simply to the thermochemical energy of two σ-bonds CC possessing two-electron charges. However, in view of the highly ordered crystal lattice of diamond, there probably exist here certain additional interactions between carbon atoms. It follows from this that there is no complete similarity between the CC bonds in diamond and in hydrocarbons. Therefore one may assume that the heat of transition of a gram-atom of diamond into carbon in that hypothetical state in which only valence forces act between its atoms, identical with those binding the carbon atoms in saturated hydrocarbons, is equal to $q \neq 0$. Thus,

$$L_C = 2(2a_{CC} + b_{CC}) + q. \tag{4}$$

Comparing (2), (3), and (4) with (1), we have:

$$a_{CC} \sum^{\frac{4n-m}{2}} A_{CC} + \frac{4n-m}{2} b_{CC} + a_{CH} \sum^{m} A_{CH} + mb_{CH} = H^{\text{el}}_{C_{nH}m} +$$

$$+ 2n(2a_{CC} + b_{CC}) + nq + mH^{\text{at}}_H$$

or, taking into account that

$$\sum^{\frac{4n-m}{2}} A_{CC} + \sum^{m} A_{CH} = 4n + m, \tag{5}$$

after obvious transformations we obtain

$$(a_{CH} - a_{CC}) \sum^{m} A_{CH} + m\left(a_{CC} - \frac{1}{2} b_{CC} + b_{CH}\right) - nq = H^{\text{el}}_{C_{nH}m} + mH^{\text{at}}_{H}. \tag{6}$$

Thus, the relation connecting the σ-electron charges of the CH bonds of the hydrocarbon $C_{nH}m$ with the experimentally determined heat of atomization of the latter contains three constants:

$$c_1 = a_{CH} - a_{CC}, \qquad c_2 = a_{CC} - {}^1\!/_2 b_{CC} + b_{CH}, \tag{7}$$

as well as q. To find them, it is simplest (and more accurate) to use three equations of type (6) for methane, ethane, and the homologous difference CH_2. To calculate A_{CH} in ethane and in CH_2 (in methane, obviously, $A_{CH} = 2$) we use the formula proposed by us earlier ([2,3])

$$A_{CH} = 1 + \frac{4}{\sum_{i=1}^{4} E_X^i}, \tag{8}$$

where E_X^i are the electronegativities of the atoms attached to the carbon atom forming the given CH bond. On the hydrogen scale $E_H = 1$, and E_C (in ethane and the CH_2 group) is equal to the ratio of the electronegativity values of carbon and hydrogen on ordinary scales ([4]), i.e. 2.5/2.1 = 1.19.

After substituting in (6) the numerical values for methane, ethane, and the CH_2 group, we obtain:

$$4 \cdot 2c_1 + 4c_2 - q = 17.889 + 4 \cdot 52.089,$$

$$6\left(1 + \frac{4}{3 + 1.19}\right) c_1 + 6c_2 - 2q = 20.236 + 6 \cdot 52.089,$$

$$2\left(1 + \frac{4}{2 + 2 \cdot 1.19}\right) c_1 + 2c_2 - q = 4.926 + 2 \cdot 52.089.$$

The solution of this system of equations gives (in kcal/mole):

$$c_1 = 26.1562, \qquad c_2 = 3.9890 \quad \text{and} \quad q = -1.0392.$$

Under the assumption that ⁽⁵⁾$b_{CC} = b_{CH} = 0$ and $q = 0$, it was found that $c_1 = 24.254$ kcal/mole and $c_2 = a_{CC} = 8.054$ kcal/mole*. As we shall see below, setting b_{CC} and b_{CH} equal to zero, although it does not affect calculations of the electronic charges of bonds from the heats of formation of hydrocarbons from the elements, nevertheless, as follows from (4), cannot be reconciled with the known data on the heat of sublimation of carbon in its various modifications.

The question of the numerical values of the coefficients a_{CC}, a_{CH}, b_{CC}, and b_{CH} is important because knowledge of them makes it possible, by means of relations (2), to calculate such theoretically interesting quantities as the thermochemical energies of σ-bonds CC and CH in different structural positions. We ourselves ⁽²⁾, and independently V. M. Tatevskii and Yu. G. Papulov ⁽⁶⁾, proposed two methods for calculating these energies, but both methods, although they lead, as we showed ⁽⁷⁾, to qualitatively coinciding results, contain assumptions introduced *ad hoc*.

To determine the coefficients a_{CC}, a_{CH}, b_{CC}, and b_{CH}, we shall use relation (7), as well as formula (4)**, which we rewrite in the form

$$a_{CC} + \frac{1}{2} b_{CC} = \frac{1}{4}(L_C - q). \tag{9}$$

Subtracting from (9) the expression for c_2 (7), we find that

$$b_{CC} - b_{CH} = \frac{1}{4}(L_C - q) - c_2. \tag{10}$$

For a judgment about the coefficients b_{CC} and b_{CH}, let us return to formulas (2). Obviously, the coefficients a_{CC} and a_{CH} must serve as a measure of the change in bond energy with a change in their electronic charge, whereas the coefficients b_{CC} and b_{CH} must characterize the constant contribution made to the energy of the C—H bond by one, and to the energy of the C—C bond by two, carbon atoms***. Then, approximately, one may assume that

$$\frac{1}{2} b_{CC} = b_{CH}. \tag{11}$$

Obviously, in contrast to b_{CC} and b_{CH}, the quantities c_1 and c_2, and consequently a_{CH} and a_{CC}, do not depend on L_C and in fact have already been obtained. Comparing (10) and (11), we find the relation

$$b_{CC} = \frac{1}{2}(L_C - q) - 2c_2. \tag{12}$$

It allows us, knowing that the heat of atomization of carbon in the form of diamond is equal to 172.151 kcal/mole ⁽⁸⁾, to determine b_{CC}, and then, from (11),

b_{CH}. The linear equations (2), after substitution of the coefficients calculated in this way, take the form:

$$\begin{aligned} Q_{CC} &= 3.9890 A_{CC} + 78.617, \\ Q_{CH} &= 30.1452 A_{CH} + 39.3085 \end{aligned} \tag{13}$$

Table 1 gives a comparison of the results of calculations of the thermochemical energies of some CC and CH bonds by formulas (13) and by the methods of works (6,7). The difference in the adopted heat of sublimation of carbon in the present work and in works (6,7), amounting to ~ 1 kcal/mole, does not hinder this comparison. From the latter the following conclusions may be drawn. First, one and the same change in the structural position of bonds affects, as shown by calculations by all three methods, in the same direction. For example, the energy of a CC bond formed by primary carbon atoms is greater than the energy of a bond formed by secondary carbon atoms. Secondly, the results of calculations by formulas (13) agree with the average energies of CC and CH bonds in normal paraffins (9), where Q_{CH} is appreciably greater than Q_{CC}, whereas in works (6,7) there is no such agreement, and for ethane, on the contrary, $Q_{\mathrm{CC}} > Q_{\mathrm{CH}}$.

Table 1

Thermochemical bond energies

Compound	Bond	Bond energy, kcal/mol: present work	Bond energy, kcal/mol: (7)	Bond energy, kcal/mol: (6)
Methane	CH	99.60	99.29	99.07
Ethane	CC	87.68	96.94	98.25
Ethane	CH	98.23	96.30	96.10
Chain $(\mathrm{CH}_2)_n$	CC	87.29	92.98	93.64
Chain $(\mathrm{CH}_2)_n$	CH	96.98	93.53	93.13

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* In work (2) the simplifying assumption $c_2 = 0$ was made and $c_1 = 28.1412$ kcal/mole and $q = -1.1154$ kcal/mole were found. However, the calculations were carried out with $F_C^{\sigma} = 1.177$. In works (5,2) a_{CC} and a_{CH} were denoted Δ_{CC}^{σ} and Δ_{CH}^{σ}.

** All equations of type (6) for hydrocarbons will not be independent.

*** From the existence of a difference in the energy of the valence and ground states of carbon atoms it follows that the thermochemical energies of bonds formed by carbon must include contributions caused not only by the distribution of the density of the valence electrons.

Having calculated the σ-electron charges of the CC and CH bonds according to the scheme indicated in (^{2}) (but taking the initial electronegativity of carbon to be 1.19, not 1.177), one can then determine, by formulas (13), the thermochemical energies of all bonds occupying different structural positions in saturated hydrocarbons. The same method can also be applied for calculating the thermochemical energies of bonds in hydrocarbon derivatives, both saturated and unsaturated.

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Note: Figure translations are in progress. See original paper for figures.

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