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## Thermochemistry of Heteroatomic Compounds: Calculation and Optimization of Bond Energies of Organic Alkanes and their Halogeno Homologues.

### Vitaly Ovchinnikov* and Alexey Kulakov.

Department of General Chemistry and Ecology, Tupolev Kazan National Researching Technical University, St-K.Marks 10, Tatarstan, Russia.

**ABSTRACT**

On the basis of the presented results is possible to come to conclusion, that the use of values of the heats of atomization of gaseous alkanes and their halogen derivatives and the use of Microsoft-Excel-function "Search of decision" for determination of the bond energy is perspective enough approach. At presence of the enough experimental or theoretical calculated data it is possible to calculate the chemical bonds in the diversified parts of organic and biochemical molecules.

**Keywords:** alkanes, halogen alkanes, heat of formation, heat of atomization, bond energy

*Corresponding author

## INTRODUCTION

In the literature a great volume data on the sizes of the energies of chemical bonds in organic compounds for today is saved up. As a rule, these data are received by a various ways: through an experimental and calculation works [1]. However, thus it is difficult enough to establish the certain conformity with law in the sizes of bond energies as they have been certain for each individual molecule.

It is necessary to note, that theoretical researchers to use, as a rule, the different approaches for the determination of bond energies in a gas phase ($E_b$). One of them is based on the equation (1), which includes the heat of atomization ($\Delta_a H^o$) and formation ($\Delta_f H^o_{mol}$) molecules, and also heats of formation in a gas phase ($\Delta_f H^o_{atom}$) all atoms making a molecule [2, 3]. The heat of atomization of a gas molecule corresponds in a first approximation to the sum of all bonds energies ($\Sigma E_b$).

$$\Delta_a H^o = \Sigma \Delta_f H^o_{atom} - \Delta_f H^o_{mol} = \Sigma E_b \qquad (1)$$

We used this approach with a following assumption: the all the same bonds have an identical magnitude in a molecule. Let's show action of this approach on some examples.

The calculation of the energy of C-H bonds of gaseous methane is very simple because of the heat of atomization of methane is equal to the sum of fours $E_{C-H}$ bonds.

We believe that in the fluoric methane derivatives the C-F bonds are broken at first and then C-H, so far as the $E_{C-H}$ is equal 440.6 but the $E_{C-F}$ is equal 460.2 kJ mol$^{-1}$. This conclusion is made on the basis of the analysis of data of work [1].

By the results of the same work [1] (Table 1) the value of C-F bond in $CF_4$ is equal 542.2 ± 4.2, in F-CHF$_2$ is equal 533.9 ± 5.9, in F-CH$_2$F is equal 496.2 ± 8.8 and in F-CH$_3$ is equal 460.2 ± 8.4 kJ mol$^{-1}$ accordingly. The similar picture is observed and for compounds with the Cl and for Br atoms (Table 5.1 and Table 5.3). Therefore we have come to conclusion, that the given hypothetical representation of atomization process can be accepted for organic molecules, in structure of which are available halogen atoms. Taking the given above it is possible to make system *i* the equations (2) and to spend optimization for the reception of minimal sum of mistakes $\Sigma R_i$, where $R_i$ there is a sum of squares of a difference between value of atomization enthalpy, calculated according to the Eq. (2) resulted in the monography [2], and the sum of bond energies in each calculated molecule.

$$[(\Delta_a H^o)_i - \Sigma(\Sigma \Delta H_{C-H}, \Sigma\Delta H_{C-C}, \Sigma \Delta H_{C-F}, \Sigma \Delta H_{C-Cl}, \Sigma \Delta H_{C-Br})_i]^2 = R_i \qquad (2).$$

## RESULTS AND DISCUSSION

The optimization was spent by the help of Microsoft-Excel program with application of the function « Search of decision » a method of the interfaced gradients. During calculations by the program has been changed the values of the bond energies of C-H, C-C, C-F, C-Cl, C-Br bonds with the purpose to minimize size $\Sigma R_i$ was automatically made [2].

Four chemical bonds C-H, C-F, C-Cl, C-Br for one carbon atom have been separately designated. For C-Cl and C-Br bonds the separate values $E_b$ in linear alkanes have been established. For the neighboring atoms of carbon, at which there were C-Cl bonds, one more variant of the bond energy has been accepted. For C-C bond energies following variants have been chosen: ClC-CCl, R-CH$_3$, R-R, R-C-Cl, R-C(R)$_{2\ or\ 3}$, where R is alkyl groups. In Table 1 results of this minimization are presented. As we see, the value of a deviation small enough no more than 2-3 %, accordingly and $\Sigma R_i$ is equal 638.4 is small size as calculations are made in kJ mol$^{-1}$ [2].

**Table 1: The results of the optimization of atomization values (kJ mol$^{-1}$) of alkanes and their halogenated derivatives.**

| Compound | $\Delta_a H_{calc}$ | $\Delta_a H_{optim}$ | $(\Delta_a H_{calc} - \Delta_a H_{optim})^2 = R_i$ |
|---|---|---|---|
| Methylfluoride, $CH_3F$ | 1732.1 | 1732.6 | 0.25 |
| Difluormethane, $CH_2F_2$ | 1802.4 | 1802.4 | 0 |
| Fluoroform, $CHF_3$ | 1881.0 | 1880.5 | 0.25 |
| Tetrafluoromethane, $CF_4$ | 1951.3 | 1951.3 | 0 |
| Methylchloride, $CH_3Cl$ | 1576.6 | 1578.2 | 2.56 |
| Dichlormethane, $CH_2Cl_2$ | 1488.1 | 1485.4 | 7.29 |
| Chloroform, $CHCl_3$ | 1401.9 | 1398.1 | 14.44 |
| Tetrachloromethane, $CCl_4$ | 1304.8 | 1299.8 | 25.0 |
| Methyl bromide, $CH_3Br$ | 1516.4 | 1514.2 | 4.84 |
| Dibrommethane, $CH_2Br_2$ | 1370.1 | 1372.9 | 7.84 |
| Bromoform, $CHBr_3$ | 1226.2 | 1230.5 | 18.49 |
| Tetrabrommethane, $CBr_4$ | 1078.2 | 1078.2 | 0 |
| Chlorotrifluoromethane, $CF_3Cl$ | 1790.1 | 1789.6 | 0.25 |
| Dichlorodifluoromethane, $CF_2Cl_2$ | 1614.4 | 1618.7 | 18.49 |
| Trichloromonofluoromethane, $CFCl_3$ | 1455.4 | 1461.6 | 38.44 |
| Bromotrifluoromethane, $CF_3Br$ | 1724.6 | 1725.7 | 1.21 |
| Dibromodifluoromethane, $CF_2Br_2$ | 1510.5 | 1506.2 | 18.49 |
| Tribromofluoromethane, $CFBr_3$ | 1300.6 | 1294.0 | 43.56 |
| Tribromochloromethane, $CClBr_3$ | 1129.9 | 1132.2 | 5.29 |
| Dibromodichloro, $CCl_2Br_2$ | 1185.8 | 1187.3 | 2.25 |
| Trichloromonofluoromethane, $CCl_3Br$ | 1234.8 | 1235.9 | 1.21 |
| Methane, $CH_4$ | 1669.1 | 1669.1 | 0 |
| n-Pentane, $C_5H_{12}$ | 6364.6 | 6367.1 | 6.25 |
| n-Hexane, $C_6H_{14}$ | 7540.8 | 7541.3 | 0.25 |
| n-Heptane, $C_7H_{16}$ | 8717.5 | 8715.5 | 4.00 |
| n-Oktane, $C_8H_{18}$ | 9894.1 | 9889.7 | 19.36 |
| n-Nonane, $C_9H_{20}$ | 11069.8 | 11063.9 | 34.81 |
| n-Propyl chloride, $C_3H_7Cl$ | 3803.5 | 3803.3 | 0.04 |
| 2-Chloropropane, $C_3H_7Cl$ | 3815.0 | 3811.5 | 12.25 |
| 1-Chlorobutane, $C_4H_9Cl$ | 4976.7 | 4977.5 | 0.64 |
| 2-Chlorobutane, $C_4H_9Cl$ | 4988.8 | 4988.5 | 0.09 |
| 2-Chloro-2-methyl-propane, $C_4H_9Cl$ | 5002.0 | 5002.0 | 0 |
| 1-Chloro-octane,       $C_8H_{17}Cl$ | 9665.0 | 9674.3 | 86.49 |
| Chloro-cyclohexane, $C_6H_{11}Cl$ | 6854.6 | 6848.6 | 36.00 |
| 1,2-Dichloroethane, $C_2H_4Cl_2$ | 2427.4 | 2429.6 | 4.84 |
| 1,1-Dichloroethane, $C_2H_4Cl_2$ | 2429.6 | 2430.4 | 0.64 |
| 1,2-dichloro-propane, $C_3H_6Cl_2$ | 3615.8 | 3621.2 | 29.16 |
| 2,2-dichloro-propane, $C_3H_6Cl_2$ | 3626.0 | 3623.3 | 7.29 |
| 1,2,3-trichloro-propane, $C_3H_5Cl_3$ | 3418.1 | 3411.9 | 38.44 |
| 1,4-dichloro-butane, $C_4H_8Cl_2$ | 4787.5 | 4784.6 | 8.41 |
| 1,2-dichloro-butane, $C_4H_8Cl_2$ | 4795.3 | 4796.8 | 2.25 |
| 1,3-dichloro-butane, $C_4H_8Cl_2$ | 4799.1 | 4800.8 | 2.89 |
| 2,3-dichloro-, (R*,S*)-, butane, $C_4H_8Cl_2$ | 4806.9 | 4810.3 | 11.56 |
| Ethylbromide, $C_2H_5Br$ | 2695.5 | 2688.2 | 53.29 |
| n-Propylbromide, $C_3H_7Br$ | 3865.8 | 3865.1 | 0.49 |
| 2-Bromo-propane, $C_3H_7Br$ | 3878.5 | 3878.5 | 0 |
| 1-Bromo-butane, $C_4H_9Br$ | 5040.9 | 5039.3 | 2.56 |
| 2-Bromo-butane, $C_4H_9Br$ | 5053.9 | 5055.4 | 2.25 |
| 1-Bromo-octane, $C_8H_{17}Br$ | 9728.1 | 9736.1 | 64.00 |
| | | | $R_i = \Sigma$ 638.4 |

The values of C-H, C-F, C-Cl, C-Br bond energies are summed in Table 2. As follows from the data of Table 2, there is a consecutive increase in the magnitudes of bond energies at methane halogen-derivatives. Thus, the values of energies of C-Cl and C-Br bonds in alkanes with the greater number of carbon atoms is much less, than at methane derivatives, that can be the confirmation, that these bonds are broken in the last turn. Thus, the average of C-Cl bond energies turns out as underestimated and with the big mistake. It is necessary to note, that received energy values of C-Hal bonds on 25-30 kJ mol$^{-1}$ is less, than resulted in the review [1].

**Table 2: The energy values of C-Hal bonds (kJ mol$^{-1}$) of the some alkanes and their halogen of derivatives**

| Bonds | C-H | C-F | C-Cl | C-Br |
|---|---|---|---|---|
| C-Cl Bonds at the neighbouring C atoms | | | 206.7 | |
| Bond in alkanes | | | 195.4 | 257.2 |
| $C_1$-Bonds | 412.9 | 476.4 | 314.4 | 260.4 |
| | 414.0 | 483.8 | 326.7 | 271.6 |
| | 419.1 | 497.2 | 326.3 | 277.7 |
| | 423.3 | 494.1 | 332.4 | 268.5 |
| The middle values | 417.3 | 487.9 | 283.7 | 267.1 |
| Standard deviation | 4.9 | 9.6 | 64.3 | 7.2 |

The values of C-C bond energies are allocated in the separate Table 3. Here it is visible, that the least value of the energy of chemical bond is observed in a carbon chain of alkanes and the greatest is for the carbon, connected with chlorine atom. It is possible to note, that the distinctions in the bond energies are not so large; the middle deviation for the energies of the bonds makes about 2-3 %.

**Table 3: The energy values (kJ mol$^{-1}$) of different types of C-C bonds**

| C-C bonds | Magnitude |
|---|---|
| ClC-CCl bonds | 362.8 |
| R-CH$_3$ | 350.3 |
| R-R | 347.5 |
| R-C-Cl | 358.5 |
| R-C(R)$_{2 \text{ or } 3}$ | 352.2 |
| Middle | 354.3 |
| Standard deviation | 6.3 |

## CONCLUSIONS

Thus, on the basis of the presented results can conclude, that the use of gas values of enthalpies atomization of alkanes and their halogen derivatives (the Microsoft-Excel-function "Search of decision" has been used) for determination of the bond energy values is perspective enough approach. At presence of the enough experimental or theoretical calculated data it is possible to calculate the chemical bonds in the diversified parts of organic and biochemical molecules.

## REFERENCES

[1] Luo, Yu-Ran. Handbook of bond dissociation energies in organic compounds. 2003; CRC PRESS. Boca Raton-London-New York-Washington, D.C.; 362 p.
[2] Dashevky VG. The conformations of organic molecules. 1974; Moskow: Khimia; 256 p.
[3] Ovchinnikov VV. American Chem Sci J 2014;4(1);1-13.