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# The Structure Dependent Energy of Organic Compounds



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# The Structure Dependent Energy of Organic Compounds

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*To Hossain Saneii  
pioneer of automation of combinatorial  
chemical syntheses*

# Preface

The subject of this book is the result of my endeavor to make organic chemistry better understood by my students. The reactions of organic compounds are influenced by two main factors. One factor is the energy of compounds the second one is their susceptibility to the attacks of reactants. The energy of organic compounds depends on their structure. It was a problem, however, that there were no data to show this dependency. The experimental heats of formation could not be applied for this purpose. This can be demonstrated by the heats of formation of some n-alkanes referring to gas state and expressed in kJ/mol.

CH <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>5</sub> H <sub>12</sub>	C <sub>7</sub> H <sub>16</sub>	C <sub>9</sub> H <sub>20</sub>
-74.9	-103.8	-146.4	-167.6	-229.0

It can be seen that there are considerable differences in the heats of formation despite the fact that these alkanes do not have specific structures that could be responsible for the differences. Only their composition differs and this is the reason of the differences in heats of formation.

The composition of isomeric compounds is the same, so the differences in their heats of formation can reflect the differences of their energy caused by differences in structure like in the case of cyclohexane and 1-hexene.

cyclohexane C <sub>6</sub> H <sub>12</sub>	1-hexene C <sub>6</sub> H <sub>12</sub>
$\Delta H_f^\circ = -123.1$	$\Delta H_f^\circ = -41.7$

Since the heats of formations in the great majority of cases do not make possible direct comparisons, the role of energy of reactants and products in the reactions is mainly neglected when teaching. Comparing the energies of unsaturated compounds by their heats of hydrogenations is an exception. As a consequence, when the reactivity of the organic compounds is considered almost exclusively their susceptibility to attacks by reagents is taking into account, and the energy factors are neglected.

In order to circumvent the problem caused by the traditional heats of formation in interpretation of the structure dependent energies of organic compounds an alternative thermochemical reference system was developed and published in 1983 [1]. The relative enthalpies replacing the heats of formation in the new system directly reflect the structure dependent energies of compounds and makes possible to compare them without any restriction. In the last three decades the relative enthalpies were successfully used in teaching organic chemistry for university students, and helped a deeper understanding of the properties of organic compounds.

Budapest, Hungary

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## Reference

1. Furka Á (1983) *Croatica Chemica Acta* 56:199.



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# Abstract

The structure-dependent energies of organic compounds are parts of the conventional heats of formation. They are masked, however, by the large energies that are evolving as the consequence of the incorporation of the constituent elements into compounds. For this reason, the heats of formation heavily depend on the composition and, as a result, only the heats of formation of isomers can be directly compared. Heats of different reactions were used in comparisons to circumvent the problem. In the case of unsaturated hydrocarbons, for example, the heats of hydrogenations were compared. None of these approaches could be generally used, so demonstration of the structure-dependent energies remained complicated.

A general approach is offered to solve the problem by modifying the conventional thermochemical reference system. In this system, the reference substances, instead of the elements, are a series of compounds: unbranched alkanes and their properly selected derivatives (halides, ethers, sulfides, and tertiary amines). The zero energy assigned to the elements, of course, is no longer sustained. Nonzero energies are derived for them that refer to a single atom. In the new reference system, the energies (relative enthalpies) of the elements are (in kJ/mol): C  $-22.83$ ,  $H_2$   $2 \times 21.724$ ,  $O_2$   $2 \times 125.85$ ,  $N_2$   $2 \times (-89.3)$ , S  $-41.626$ ,  $F_2$   $2 \times 198.0$ ,  $Cl_2$   $2 \times 47.11$ ,  $Br_2$   $2 \times 4.08$ , and  $I_2$   $-2 \times 53.8$ .

The "relative enthalpies" of compounds that replace the heats of formation in the new system are calculated by adding to the heats of formation the relative enthalpies of the constituent elements multiplied by the number of their atoms in the molecule. The relative enthalpies express the structure-dependent relative energies of compounds and can be compared to each other without restrictions.

As examples, the relative enthalpies of selected representatives of the following types of compounds are presented: alkanes and cycloalkanes, alkenes and cycloalkenes, polyolefins and cyclic polyolefins, aromatic hydrocarbons, alcohols and phenols, ethers, peroxides, aldehydes and ketones, acetals, carboxylic acids, esters and anhydrides, alkyl, alkenyl and aryl halides, carboxylic acid halides, carbonyl halides, amines, carboxylic acid amides, hydrazine derivatives, nitriles, heteroaromatic compounds, nitro-compounds, organic nitrites and nitrates, organic sulfides, thiols, disulfides, sulfoxides, sulfones, organic sulfites, sulfates, selected

inorganic compounds, organic radicals, organic cations and organic anions. Estimated stabilization energies of conjugated olefins, benzene, furan, pyrrole, and thiophene are also presented. The contribution of the transformed and newly formed compounds to the heats of reactions is also discussed.

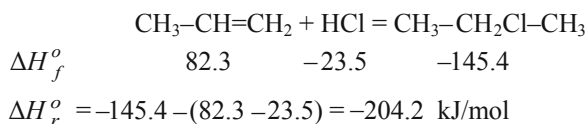
# Chapter 1

## An Alternative Thermochemical Reference System



### 1.1 Introduction

The chemical compounds have energies that depend on their composition and structure. The absolute values of these energies are not known. The quantities that can be really measured are the heats of their reactions. The heat of reaction expresses the energy of the reaction products relative to that of the reactants. The traditional heats of formation coming out from these measurements are also relative values that compare the energy of compounds to the energies of arbitrarily selected reference substances. The reference substances are the elements that build up the compounds. By definition, the heats of formation of the elements are zero. Considering the elements as reference substances is a logical choice since the compounds are built up from elements. The heats of formation ( $\Delta H_f^\circ$ ) work perfectly for example in calculating the heat of any reaction ( $\Delta H_r^\circ$ ) if the heats of formation of both reactants and products are known. The heat of reaction can be calculated by subtracting the heats of formation of the reactants from the sum of the heats of formation of the products. Here is an example. Both reactants and the product are in gas phase [1, 2].



It can be shown, however, that instead of zeros any other value can be assigned to the elements, and the result of calculation of the heat of reaction remains unchanged.

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**Electronic Supplementary Material** The online version of this chapter ([https://doi.org/10.1007/978-3-030-06004-6\\_1](https://doi.org/10.1007/978-3-030-06004-6_1)) contains supplementary material, which is available to authorized users.