

Comparison of the Heats of Formation[‡] of Hydrocarbons*

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In order to facilitate the demonstration of the structure dependent stabilizing or destabilizing energy effects characterizing the individual hydrocarbons it is suggested to replace graphite and hydrogen as reference substances (used in calculating the heats of formation) by the series of n-alkanes. This can be achieved by converting the heats of formation into relative enthalpies (H_{rel}). The proposed simple equation yields zero for the H_{rel} of n-alkanes and thus the extra stabilizing or destabilizing effects caused for example by branching or unsaturation, respectively, in other types of compounds are directly expressed by the numerical value of their H_{rel} .

When teaching organic chemistry it is often needed to demonstrate the structure dependent stabilizing or destabilizing effects. For this purpose either the heats of formation (ΔH_f) or the heats of properly chosen reactions — for example heats of hydrogenation — are compared. It has to be taken into account, however, that a considerable fraction of the ΔH_f of a compound is arising from the mere combination of its constituent elements (since the elements are the reference substances) and this part often masks the contribution of the structural differences. ΔH_f is strongly dependent on composition and, as a consequence, comparisons are meaningful only when isomers are concerned. Heats of hydrogenation can be used to compare to one another the stability of different alkenes regardless of their composition. They do not really express, however, the stability difference between an alkene and its saturated derivative**.

The purpose of this paper is to show that in the case of hydrocarbons the disturbing effect due to the differences in composition can be eliminated by replacing carbon and hydrogen as reference substances by n-alkanes. This can be realized by converting ΔH_f of the hydrocarbons into relative enthal-

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‡ Heats of formation and heats of reaction mean enthalpies of formation and enthalpies of reaction, respectively. The data taken from three sources^{1,2,3} refer to gas phase and are expressed in kJ/mole.

** The heat of hydrogenation in fact represents the difference between the ΔH_f values of the two compounds which, however, are not isomers.

pies* (H_{rel}) defined by the following equation**, where n_{C} and n_{H} are the number of carbon and hydrogen atoms, respectively.

$$H_{\text{rel}} = \Delta H_{\text{f}} - 22.822 n_{\text{C}} + 21.72 n_{\text{H}}$$

H_{rel} values calculated from ΔH_{f} of several representatives of different classes of hydrocarbons are summarized in Tables I and II. These data show

TABLE I
Relative Enthalpies of Some Acyclic Hydrocarbons^a

	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇
n-alkanes	0	1	0	0	0	0
2-Me-alkanes		-9	-8	-7	-7	-7
2,2-diMe-alkanes		-19	-18	-18	-16	-18
1-alkenes	93	82	82	82	82	82
konj. polyenes			149		207	
1-alkynes	225	204	204	204	204	204

^a Data in kJ/mole, C₂—C₇: number of carbon atoms in the unsubstituted chain, Me: methyl, H_{rel} of methane not included above: -11.

TABLE II
Relative Enthalpies of Some Cyclic Hydrocarbons

	H_{rel} kJ/mole		H_{rel} kJ/mole
cyclopropane	115	benzene	76
cyclobutane	109	naphthalene	97
cyclopentane	26	azulene	225
cyclohexane	1	anthracene	129
cycloheptane	25	phenanthrene	105
cyclohexene	75	triphenylene	109
1,3-cyclohexadiene	145	tetracene	142
cyclooctatetraene	289	perylene	113

that the structural effects like stabilization due to branching or destabilization caused by unsaturation or ring strain are directly expressed by the numerical value (including sign) of H_{rel} . It is important to note that H_{rel} does not depend on chain length or on composition and consequently H_{rel} values of non-isomers can be compared to one another without difficulty. The possibility of such comparisons is particularly important when more than one structural effect is operating in the molecule.

Preliminary studies show that the use of relative enthalpies in teaching can be extended to all classes of organic compounds, and in addition, they are expected to facilitate the comparison with the experimental data of some theoretically deduced quantities such as the different types of resonance energies.^{4,5,6}

* The heats of formation themselves can be considered as relative enthalpies, too.

** The constants were determined by the least-squares method from ΔH_{f} of n-alkanes.

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SAŽETAK

Usporedba toplina stvaranja ugljikovodika

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Radi lakše demonstracije stabilizirajućih ili destabilizirajućih energijskih efekata ovisnih o strukturi, koji karakteriziraju pojedine ugljikovodike, predložena je zamjena grafita i vodika kao referentnih supstancija (za izračunavanje toplina stvaranja) nizom n-alkana. To se može postići preračunavanjem toplina stvaranja u relativne entalpije (H_{rel}). Predložena jednostavna jednadžba daje nulu za H_{rel} n-alkana, i njome su posebni stabilizirajući ili destabilizirajući efekti, uzrokovani na primjer grananjem ili nezasićenjem u drugim tipovima spojeva, izraženi numeričkom vrijednošću njihove H_{rel} .