Bond Energies of the Hydrocarbons: Corrections Yielding Additivity

V. Deitz

LETTERS TO THE EDITOR

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Zahn[1] has recently proposed an additional interaction energy between hydrocarbon bonds in order to account for the non-additivity of the bond energies of hydrocarbons. Some such treatment appears justified in view of the excellent data of Rossini[2] who has determined the heats of combustion of the normal aliphatic hydrocarbons with sufficient accuracy to detect deviations from additivity among the first members of the series. Also, to account for the existing data for other compounds, Pauling and Sherman[3] have proposed a resonance energy between certain isomeric configurations; for example, the two Kekulé structures of benzene.

In this note attention is directed to the possibility of attaining bond additivity by simply applying the following corrections: (1) Zero-point vibrational energy of each particular molecule; (2) a cross-interaction between the hydrogen atoms attached to the same carbon atom; (3) referring the heats of dissociation into atoms to $0°K$. The results are in Table I. All energies are in kilocalories.

TABLE I.

	V_0'	ϵ_0	V_0 Exp.	Number of Bonds				V_0 Calc.	Per-cent devia-tion
				C—H	H..H	C—C	C=C		
CH_4	356.7	27.3	384.0	4	6	0	0	384.0	——
C_2H_6	595.9	44.2	640.1	6	6	1	0	640.1	——
C_3H_8	837.4	61.7	899.1	8	7	2	0	899.2	+0.01
C_4H_{10}	1079.4	78.4	1157.8	10	8	3	0	1158.3	+0.04
C_5H_{12}	1321.3	96.6	1417.9	12	9	4	0	1417.4	−0.03
C_6H_{14}	1563.5	116.9	1680.4	14	10	5	0	1676.5	−0.23
C_7H_{16}	1805.7	135.1	1940.8	16	11	6	0	1935.6	−0.26
C_8H_{18}	2047.8	150.7	2198.5	18	12	7	0	2194.7	−0.17
C_2H_4	469.3	33.4	502.7	4	2	0	1	502.7	——
C_6H_6	1101.8	62.0	1163.8	6	0	3	3	1160.4	−0.28
				.6	0	9	0	1206.9	+3.78
C_6H_{10}	1329.6	91.7	1421.3	10	4	5	1	1423.2	+0.13
C_6H_{12}	1451.1	111.0	1562.1	12	6	6	0	1554.6	−0.48

For the reaction $C_mH_n(g) \rightarrow mC(g) + nH(g)$ one need only consider the zero-point energy of the hydrocarbon, for that of the compounds used in the auxiliary chemical equations cancels. In calculating this energy for the aliphatic hydrocarbons the frequencies used are from Kohlrausch and Köppel,[4] and those for cyclohexane, cyclohexene and benzene are also from recent work.[5] This zero-point energy, $\epsilon_0 = \Sigma_i h\nu_i/2 = \Sigma_i [.00142\bar{\nu}_i(cm^{-1})]$ kcal. per mole is an appreciable factor, as shown from Table I. This energy is distributed over the whole molecule and cannot be said to reside in any particular bonds.

The value of 136.5 kcal. was used for the heat of vaporization of carbon. This figure was calculated from the recent work of Lozier,[6] who slightly favors this value over an alternate value of 182.0 kcal. However, the absolute value is not significant in this calculation; any reasonable value used consistently throughout would serve the same pur-

pose. The heats of dissociation of H_2O into H_2 and O_2, of CO_2 into graphite and O_2, and of H_2 into hydrogen atoms were taken as 68.31, 94.24 and 102.9 kcal., respectively. The heats of combustion are from the work of Rossini[2] or from the table compiled by Kharasch. The corrections to $0°K$ were made for the hydrocarbons by the use of the same frequencies from which the zero-point energies were calculated. The change in heat content of the hydrogen atoms from 298° to $0°K$ was calculated. The uncertainties in the heat of vaporization of carbon are more than sufficient to absorb the correction of the carbons to $0°K$. It turned out that the results were not very sensitive to these corrections to $0°K$.

In Table I, V_0' is the heat of dissociation of the hydrocarbons into gaseous atoms at $0°K$, and V_0 is the sum of ϵ_0 and V_0'. It is the sum that gives the total depth of the potential energy valley.

A cross-interaction between the hydrogens of 3.0 kcal. attraction is proposed. This is frankly an empirical correction factor. There are probably several ways of accounting for this value, perhaps the simplest being the predominating van der Waals energy of attraction. One need only consider the pairs of hydrogens attached to the same carbon atom, for the other hydrogens are too far removed from each other to contribute effectively.

Using the value of 3.0 kcal. attraction for H . . . . H, the C—H bond, as obtained from methane, equals 91.5 kcal.; the C—C bond, as obtained from ethane, equals 73.1 kcal.; the C=C bond, as obtained from ethylene, equals 130.7 kcal.

The first point to observe from an examination of Table I is that all of the aliphatic hydrocarbons have additive bond energies to within the accuracy of the data available. This accounts for the deviations reported by Rossini. The second and most important point is that benzene has a heat of dissociation equal to the sum of $6(C-H)$, $3(C-C)$ and $3(C=C)$ bonds. This suggests that it is not certain that resonance energy is as important as has been supposed. The data available are such as to make any final decision on this point premature. Finally, it is to be noted that cyclohexane and cyclohexene indicate further the consistency of this analysis.

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V. DEITZ*

University of Illinois,
   Urbana, Illinois,
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* National Research Fellow.
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