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Abstract

Full Text

CHEMISTRY

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SOME REFINEMENT OF THE VALUES OF THE CONSTANTS IN V. M. TATEVSKII' S SCHEME FOR CALCULATING THE HEATS OF COMBUSTION OF ALKANES

(Presented by Academician A. A. Balandin, 16-IX-1960)

For calculating a number of physicochemical properties of alkanes, in particular their heats of combustion, several additive schemes have now been proposed (1-11). One of the most consistent, and one that gives good agreement with experimental data, is the scheme proposed by V. M. Tatevskii (6).

In this scheme all C-C and C-H bonds in an alkane molecule are distinguished according to whether the carbon atoms participating in them are primary (C₁), secondary (C₂), tertiary (C₃), or quaternary (C₄). Thus, ten subtypes of carbon-carbon bond are possible: C₁-C₁ (only in ethane), C₁-C₂, C₁-C₃, C₁-C₄, C₂-C₂, C₂-C₃, C₂-C₄, C₃-C₃, C₃-C₄, C₄-C₄, and three subtypes of C-H bond: C₀-H (only in methane), C₁-H, C₂-H, C₃-H.

The numerical value of certain physicochemical properties of an alkane (refractive index, molecular volume, heat of combustion and formation, etc.) can be obtained by summing certain constants—“contributions”—assigned to the listed subtypes of carbon-carbon bonds (the “contributions” of C-H bonds in this scheme are distributed among the “contributions” of C-C bonds).

The numerical values of the “contribution” constants assigned to each bond can be found by comparing the corresponding equations with experimental data.

We give the values of the contributions of the corresponding bonds calculated by V. M. Tatevskii for calculating the heats of combustion (at 25°) of alkanes in the gaseous and liquid states:

Bond subtypes	C ₁ -C ₂	C ₁ -C ₃	C ₁ -C ₄	C ₂ -C ₂	C ₂ -C ₃	C ₂ -C ₄	C ₃ -C ₃	C ₃ -C ₄	C ₄ -C ₄
Contributions	106,038	226,993	208,679	156,231	120,454	102,696	85,551	68,904	—
liquid									
uid									

Bond sub-types	C ₁ —C ₂	C ₁ —C ₃	C ₁ —C ₄	C ₂ —C ₂	C ₂ —C ₃	C ₂ —C ₄	C ₃ —C ₃	C ₃ —C ₄	C ₄ —C ₄
Contributions, kcal/mole	265,17	228,48	210,01	157,41	121,35	103,35	86,45	69,40	53,22
gas									

Here the contribution of the C₄—C₄ bond is absent for calculating the heat of combustion of alkanes in the liquid state. At the time the scheme was drawn up, the author had no experimental data for any alkane in whose molecule there would be a C₄—C₄ bond and whose heat of combustion in the liquid state would be known.* As for the contribution of the C₄—C₄ bond for calculating the heat of combustion of alkanes in the gaseous state, this quantity was calculated by the author of the scheme on the basis of the only experimental value then available for the heat of combustion of 2,2,3,3-tetramethylbutane. V. M. Tatevskii noted^(6,18) the low reliability of this value, since the heat of combustion of this substance was experimentally determined for the solid state⁽¹³⁾, and its heat of combustion in the gaseous state was calculated taking into account an estimate of its heat of sublimation⁽¹⁴⁾.

We measured the heat of combustion at 25° of 2,2,3,3-tetramethylhexane in the liquid state; its value was found to be 1619.1 ± 0.5 kcal/mole.**

* The work of Johnson, Prosen, and Rossini⁽¹²⁾, in which the heat of combustion of 2,2,3,3-tetramethylpentane is reported, was used by V. M. Tatevskii only in his last publication⁽¹⁸⁾.

** The method for determining the heat of combustion, and the synthesis and purification of the substance, are analogous to those described in^(15,16).

Using this value and the previously determined magnitude of the heat of combustion of 2,2,3,3-tetramethylpentane⁽¹²⁾, we were able to calculate the contributions of the C₄—C₄ bond for calculating the heat of combustion of alkanes both in the liquid and in the gaseous state.

Table 1

Compound from which the value was found	Contribution of the C ₄ —C ₄ bond (liquid)	Contribution of the C ₄ —C ₄ bond (gas)
2,2,3,3-Tetramethylhexane	53.55	54.26*
2,2,3,3-Tetramethylpentane	53.77	54.32
2,2,3,3-Tetramethylbutane	—	(53.22)**
Average...	53.66	54.29

* The heat of vaporization was calculated by us from a semiempirical relation⁽¹⁷⁾.

** Taken from the work of V. M. Tatevskii⁽⁶⁾.

Table 1 gives the results of this calculation.

From Table 1 it is seen:

1. The values of the C_4-C_4 bond contributions for calculating the heat of combustion of alkanes both in the liquid and in the gaseous state, calculated from the data obtained in the present work (from the heat of combustion of 2,2,3,3-tetramethylhexane), agree with their values found from the data of work⁽¹²⁾ (from the heat of combustion of 2,2,3,3-tetramethylpentane). The deviation by ~ 1 kcal of the value given for this contribution in Tatevskii's work should apparently be attributed to an inaccuracy in estimating the heat of sublimation of this substance.
2. At present the most reliable values of the C_4-C_4 bond contribution should be regarded as 53.66 kcal/mol for calculating the heat of combustion of alkanes in the liquid state and 54.29 kcal/mol for calculating the heats of combustion of alkanes in the gaseous state.

The values obtained make it possible to calculate the heats of combustion of all alkanes having C_4-C_4 bonds in the molecule.

Using one of these values (53.66 kcal/mol), we were able to compare the experimental value found by us for the heat of combustion of 2,2,3,3,5,5,6-heptamethylheptane (2248.4 ± 0.4 kcal/mol) with that calculated according to the additive scheme of V. M. Tatevskii (2247.7 kcal/mol).^{*} As can be seen from the numbers given, the agreement proved satisfactory.

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* In this calculation a correction of 5 ± 1 kcal/mol was introduced, allowing for the presence in the alkane molecule of a grouping of two quaternary carbon atoms separated by one CH_2 group. For the argumentation of this correction, see work ⁽¹⁹⁾.

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

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