M. P. Kozina, A. K. Mirzaeva, I. E. Sosnina, N. V. Elagina, S. M. Skuratov

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Abstract

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M. P. Kozina, A. K. Mirzaeva, I. E. Sosnina, N. V. Elagina, S. M. Skuratov

HEAT OF FORMATION OF SPIROCYCLOALKANE HYDROCARBONS*

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For certain classes of hydrocarbons, several calculation schemes have now been proposed ($^{1-3}$), by means of which it is possible, with one or another degree of accuracy, to calculate in advance the values of many physicochemical constants, in particular heats of formation. In principle, all these schemes are based on summing the "contributions" made to the numerical value of the given property by individual structural elements of the molecule (atoms, groups of atoms, bonds, etc.). The magnitudes of these contributions—constants—are found on the basis of available experimental data. Moreover, the greater the accuracy claimed by a given scheme, the greater the number of corresponding constants used in it (allowance for various interactions of neighboring or nearby bonds, mutual influences of chemically unbonded atoms, and other subtle features of structure). An attempt to extend a calculation scheme to a new class of compounds requires the introduction into it of constant quantities that can be found only on the basis of data for compounds of this class. For calculating the heats of formation of hydrocarbons of spiro structure, none of the proposed schemes could be used, since among compounds of this series only the heat of combustion of spiropentane had been experimentally determined (^{4}). However, the authors of that work point out that the result obtained by them should be regarded as preliminary, since the high volatility of spiropentane caused difficulties in its combustion and the average result was obtained from only three experiments. Therefore this value was not included by us in the discussion.

In the present work the heats of combustion have been determined experimentally and, from them, the heats of formation calculated for the following spiro hydrocarbons:

Name of compound	Formula	Ring combination
Spiro-(4,4)-nonane	C_9H_{16}	5–5
Spiro-(4,5)-decane	$C_{10}H_{18}$	5–6
Spiro-(5,5)-undecane	$C_{11}H_{20}$	6–6
Spiro-(5,6)-dodecane	$C_{12}H_{22}$	6–7

The synthesis and purification of the substances studied were carried out in the laboratories of the Departments of Petroleum Chemistry and Organic Catalysis of Moscow State University and are described in the corresponding works ($^{5-8}$).

Table 1 gives the physicochemical constants of the substances studied.

Table 1

Compound	Boiling point, °C; pressure, mm Hg	d_4^{20}	n_D^{20}	$\frac{CO_2\ \text{found}}{CO_2\ \text{calculated}}$
C_9H_{16}	156.5–157/757	0.8621	1.4619	0.9993 ± 0.032
$C_{10}H_{18}$	84.5–85.3/31.5	0.8774	1.4711	1.0001 ± 0.035
$C_{11}H_{20}$	89/15	0.8887	1.4789	0.9996 ± 0.035
$C_{12}H_{22}$	100–101/9	0.9021	1.4874	1.0004 ± 0.031

The same table gives the ratio of the amount of CO_2 determined in the calorimetric experiments to the amount of CO_2 calculated from the initial weighed portion of the substance. This ratio can, to a certain extent, serve as a criterion of the purity of the substance and of the completeness of its combustion reaction. As can be seen from the data of Table 1, for all the substances investigated the ratio is very close to unity.

The calorimetric apparatus and the method for measuring heats of combustion are described in papers (^{9}, ^{10}). The heat value of the calorimetric system was determined by burning standard benzoic acid. Its heat of combustion under standard conditions was taken as 6318.1 cal/g (weight in vacuum, 1 cal = 4.1840 J). The temperature of the calorimeter was measured with a platinum resistance thermometer ($R_0 = 50$ ohms) and could be read to an accuracy of 0.0001°. A detailed description of the simplified bridge circuit used in the present work for measuring the resistance of the platinum thermometer, and of the method for calculating the temperature rise in an experiment, is given in (^{11}). The average values obtained for the heats of combustion and the heats of formation calculated from them are presented in Table 2.

Table 2

Compound(in the liquid state)	$-\Delta H^{25}_{\text{comb}}$,kcal/mol	$-\Delta H^{25}_{\text{form}}$,kcal/mol
C_9H_{16}	1358.6 ± 0.3	34.4 ± 0.3
$C_{10}H_{18}$	1507.5 ± 0.3	47.9 ± 0.3

* Trainee from the PRC Liu Qin-xian took part in the experimental work.

Compound(in the liquid state)	$-\Delta H^{25}_{\text{comb}}$,kcal/mol	$-\Delta H^{25}_{\text{form}}$,kcal/mol
$C_{11}H_{20}$	1658.4 ± 0.5	59.3 ± 0.5
$C_{12}H_{22}$	1819.6 ± 0.2	60.5 ± 0.2

The mean value of the quantities was obtained from no fewer than six experiments. The error of the results in ΔH_{comb} is given as twice the quadratic error of the mean result (2S). In ΔH_{form} the error is given as

$$2\sqrt{S^2 + n(S')^2 + m(S'')^2},$$

where S' and S'' are the errors in the heats of formation of CO_2 and H_2O, and n and m are the numbers of moles of these substances obtained on combustion of the given compound. In calculating the standard heats of formation of the spiranes, ΔH_{form} of CO_2 and H_2O were taken, respectively, as ([12]) 94.0517 ± 0.0108 and 68.3149 ± 0.0096 kcal/mol (with allowance for the atomic weights of 1961).

As indicated above, none of the calculation schemes claiming high accuracy can be used for calculating hydrocarbons of spirane structure. However, if one proceeds from the fact that in the study of the structure of spiropentane both the C–C and C–H bond lengths and the CCC and HCH angles in it were found ([13]) to be very close to those in cyclopropane, and extends this conclusion to other spiranes, i.e., assumes that the geometry of the rings in spiranes is the same as in the corresponding cyclanes, then the heat of combustion (or the standard heat of formation) of spirane hydrocarbons can be approximately calculated by the following formula:

$$-\Delta H^{25}_{\text{comb(l)}} = A + nB + \sum C, \tag{1}$$

where A is the increment contributed to the given property of the spirane by the quaternary carbon atom; B is the increment contributed by each $-CH_2-$ group; n is the number of these groups in both rings of the spirane hydrocarbon. $\sum C$ is the sum of the "cyclization enthalpies" of the rings forming the given spirane. (By cyclization enthalpy, as in our other works, is meant the difference between the heat of combustion of the corresponding cyclane and the quantity $B \times m$, where m is the number of $-CH_2-$groups in the cyclane, and B is the contribution to the heat of combustion of the $-CH_2-$group in any normal alkane with the number of carbon atoms $C > 4$.)

The value A can be found on the basis of the experimental data obtained in the present work. The value B is known from the heats of combustion (or heats of formation) of normal alkanes in the liquid state and is equal to 156.23 kcal/mol (or 6.12 kcal/mol for the heat of formation) ([12]).

The values C—the cyclization enthalpies for cyclanes in the liquid state—may be taken, from experimental data ([14], [15]), as equal to:

for cyclopentane $786.66 - 156.23 \times 5 = 5.5$ kcal/mole,

for cyclohexane $936.57 - 156.23 \times 6 = -0.8$ kcal/mole,

for cycloheptane $1098.85 - 156.23 \times 7 = 5.2$ kcal/mole.

Below is the calculation of the value A for all four spirans investigated in the present work.

$$\begin{array}{lll} \text{Spirane} & & \\ C_9H_{16} & A_1 & = 1358.6 - 8 \times 156.23 - 5.5 \times 2 = 97.8 \\ C_{10}H_{18} & A_2 & = 1507.5 - 9 \times 156.23 - 5.5 + 0.8 = 96.7 \\ C_{11}H_{20} & A_3 & = 1658.4 - 10 \times 156.23 + 0.8 \times 2 = 97.7 \\ C_{12}H_{22} & A_4 & = 1819.6 - 11 \times 156.23 - 5.2 + 0.8 = 96.6 \\ & & \text{Mean value } A_{\text{av}} = 97.2 \pm 0.5 \text{ kcal/mole} \end{array}$$

The fact that the values of A in all four cases proved to be quite close indicates that the assumptions adopted in using formula (1)—the preservation of the cyclization enthalpy characteristic of the given monocyclic ring in the corresponding rings forming the spirane; and the constancy of the increment of the quaternary carbon atom entering into the spirane molecule—are justified with sufficient approximation.

Thus, substituting $A = 97.2$ kcal/mole into formula (1), it can be recommended for calculating the heats of combustion of spiranes:

$$-\Delta H^{25}_{\text{comb}(l)} = 97.2 + 156.23n + \Sigma C.$$

It is interesting to note (this is also an argument in favor of the applicability of the proposed calculation formula) that the value $A = 97.2$ is very close to the increment contributed by a quaternary atom to the heat of combustion of alkanes with long side chains (for example, for 4-ethyl-4-*n*-propylheptane the value $A = 98.2$ kcal/mole).

When calculating the standard heats of formation of liquid spirocyclanes by formula (1), one should use, found in an analogous manner, the following values of the increments: $A = -3.0$ kcal/mole, $B = 6.12$ kcal/mole, while C retains the same values as indicated above but has the opposite sign.

$$-\Delta H^{25}_{\text{form}(l)} = -3.0 + 6.12n - \Sigma C.$$

The error in the values of the heats of combustion or formation obtained by calculation using formula (1) is unlikely to exceed 1–1.5 kcal/mole.

Moscow State University
named after M. V. Lomonosov

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

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