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**Abstract**

**Full Text**

**CHEMISTRY**

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## **HEATS OF COMBUSTION OF 1,1-DIMETHYL- 2-ALKYLCYCLOPROPANES**

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The availability of accurate experimental data on the heats of combustion of certain alkylcyclohexanes and alkylcyclopentanes has made it possible to calculate, with sufficiently high accuracy, the heats of combustion and formation of the remaining members of the corresponding homologous series, containing both normal and branched side chains (<sup>1,2</sup>). For cyclopropane hydrocarbons such calculations could not until recently be made, since accurate experimental data on their heats of combustion were practically lacking. A reliable value exists only for the heat of combustion of gaseous cyclopropane (<sup>3</sup>). The remaining data are not very reliable (<sup>4-6</sup>). Meanwhile, thermochemical data on cyclopropane hydrocarbons are of great theoretical and practical interest.

In the present work we report the results of determining the heats of combustion of three 1,1-dimethyl-2-alkylcyclopropanes in the liquid phase and give formulas for calculating the heats of combustion of all compounds of this homologous series. The method used for determining the heats of combustion has been described in detail earlier (<sup>7</sup>). A calorimeter with an isothermal jacket was used. Liquid substances sealed in thin-walled glass ampoules were burned in a calorimetric bomb, in an excess of oxygen, at an initial experimental temperature of 25°. A mercury thermometer was used for temperature measurement; temperature readings were made with an accuracy of  $3 \cdot 10^{-4}^{\circ}$ . The thermal value of the calorimeter was determined with benzoic acid, whose heat of combustion was taken as 6322.8 cal/g (weight in air) at 25° (1 cal = 4.1840 abs. J.). An iron wire was used to ignite the substance. The heats of formation of  $\text{Fe}_2\text{O}_3$  and of the nitric acid solution in the bomb were taken to be 1793 cal/g and 13.80 kcal/mole, respectively. The sample weight was, as a rule, determined from the difference between the weight of the empty and the filled ampoule with an accuracy up to  $2 \cdot 10^{-5}$  g and ranged from 0.2 to 0.3 g. In the case of the low-boiling 1,1-dimethyl-2-ethylcyclopropane, the weight of the burned substance was found from the results of analysis of the combustion products for  $\text{CO}_2$ . The substances were synthesized and purified by the previously described method (<sup>8</sup>). Raman spectra showed the absence of alkene impurities in the preparations.

**1,1-Dimethyl-2-ethylcyclopropane**,  $\text{C}_7\text{H}_{14}$  (mol. wt. 98.189). The prepa-

ration was purified by threefold and fourfold distillation over metallic sodium. After the last distillation the constants of the substance remained unchanged: b.p. 78.75°/746;  $d_4^{20}$  0.7105;  $n_D^{20}$  1.3960; results of microanalysis (in %): C 85.95; H 14.12. (Theoretical for all three compounds: C 85.63; H 14.37.)

**1,1-Dimethyl-2-propylcyclopropane**,  $C_8H_{16}$  (mol. wt. 112.216). After fivefold and sixfold distillation over metallic sodium the preparation had the following constants: b.p. 105.5°;  $d_4^{20}$  0.7297;  $n_D^{20}$  1.4060. Microanalysis gave (in %): C 85.96; H 14.17.

1,1-Dimethyl-2-*n*-hexylcyclopropane,  $C_{11}H_{22}$  (mol. wt. 154.297). After the fourth and fifth distillations the constants of the substance were as follows: b.p. 176.5°/736,  $d_4^{20}$  0.7612;  $n_D^{20}$  1.4240. As a result of microanalysis, found (%): C 85.74; H 14.32.

**Table 1**

Heats of combustion of 1,1-dimethyl-2-*n*-alkylcyclopropanes,  $-\Delta H_c^0$ , at 25° and 1 atm, in kcal/mole

1,1-Dimethyl-2-ethylcyclopropane	1,1-Dimethyl-2-propylcyclopropane	1,1-Dimethyl-2-hexylcyclopropane*
Threefold distillation	Fivefold distillation	Fourfold distillation
1115.5	1271.2	1740.3
1115.2	1271.2	1739.9
1115.0	1272.6	1739.4
1114.6	1270.8	1740.0
1114.7	1270.4	
Fourfold distillation	Sixfold distillation	Fivefold distillation
1115.1	1271.2	1739.7
1115.0	1271.1	1741.4
1114.9	1271.1	1739.7
		1739.9
1115.0 ± 0.2** (±0.02%)	1271.2 ± 0.4 (±0.03%)	1739.9 ± 0.4 (±0.03%)

\* Table 1 gives nine experiments out of nineteen, since in the others incomplete combustion was found.

\*\* In all data presented in this work, the error is indicated as the mean deviation from the arithmetic mean.

Table 1 gives the data on the determination of the heats of combustion of the three compounds listed after the last two distillations. From the data presented it is evident that for all three substances the heat of combustion, after the final distillation, did not change within the accuracy of the determinations.

Using the additive method and the concepts of the types and subtypes of bonds developed by V. M. Tatevskii (<sup>1,2</sup>), the general formula for calculating the heats

of combustion of 1,1-dimethyl-2-alkylcyclopropanes may be represented in the following form:

$$-\Delta H_{C_nH_{2n}} = c' + \sum n_{ij}A_{ij}, \quad (1)$$

where  $c'$  is the increment of the heat of combustion attributable to the sum of bonds in the group



$\sum n_{ij}A_{ij}$  refers to the bonds in the substituent alkyl radical, normal or branched. For 1,1-dimethyl-2- $n$ -alkylcyclopropanes (alkyl—any radical beginning with ethyl, i.e., at  $n \geq 7$ ), equation (1) takes the form:

$$\Delta H_{C_nH_{2n}} = c' + \sum n_{ij}A_{ij} = I_{23'} + I_{2'4'} + I_{3'4'} + 2y_{14'} + y_{23'} + (n-7)A_{22} + A_{21}, \quad (2)$$

where  $I_{ij}$  are coefficients referring to bonds in the ring, and  $y_{ij}$  to ring-side-chain bonds (together making up  $c'$ ). The remaining terms refer to bonds in the substituent  $n$ -alkyl and are included in the sum  $n_{ij}A_{ij}$ . There are as yet insufficient experimental data for calculating  $I_{ij}$  and  $y_{ij}$ , but  $A_{22}$  and  $c'$  can be calculated from the data obtained in the present work. The value of  $A_{22}$  found by us from the heats of combustion of 1,1-dimethyl-2-ethyl- and 1,1-dimethyl-2- $n$ -hexylcyclopropane,

$$A_{22} = \frac{1}{4}(1739.9 - 1115.0) = 156.23 \text{ kcal/mole},$$

coincides with the literature value 156.231 kcal/mole found for alkanes, alkylcyclopentanes, and alkylcyclohexanes<sup>(1)</sup>. The same agreement of the coefficient  $A_{22}$  for compounds of this series was obtained in calculations by the same scheme for other physicochemical properties, such as heat of formation ( $-\Delta H_f^0$ ), molecular refraction ( $R_M$ ), and molar volume ( $V_M$ ). Table 2 gives examples of such agreement.

From the data on the heats of combustion of 1,1-dimethyl-2-ethyl- and 1,1-dimethyl-2-hexylcyclopropane and the value found for  $A_{22}$ , the heats of combustion of 1,1-dimethyl-2-propyl-, 1,1-dimethyl-2- $n$ -butyl-, and 1,1-di-

methyl-2- $n$ -amylcyclopropane. The heats of combustion of the compounds listed ( $-\Delta H_c^0$ ) and their heats of formation ( $-\Delta H_f^0$ ) are given in Table 3. For the calculation of  $-\Delta H_f^0$ , the values  $-\Delta H_f^0(\text{CO}_2(\text{g})) = 94.052 \text{ kcal/mol}$  and  $-\Delta H_f^0(\text{H}_2\text{O}(\ell)) = 68.317 \text{ kcal/mol}$  were used.

As can be seen from the data presented, the calculated and experimental values for the heat of combustion of 1,1-dimethyl-2-propylcyclopropane proved to be in agreement.

Table 2

	$-\Delta H_c^0$ , Coefficient exp.	$-\Delta H_c^0$ , lit.	$-\Delta H_f^0$ , exp.	$-\Delta H_f^0$ , lit.	$R_M$ , exp.	$R_M$ , lit.	$V_M$ , exp.	$V_M$ , lit.
$A_{22}$	156.23	156.23†	6.13	6.138	4.64	4.643	16.27	15.96
$c'$	851.74	—	6.96	—	25.49	—	96.86	—

Table 3

Heats of combustion and heats of formation of 1,1-dimethyl-2-*n*-alkylcyclopropanes at 25 °C and 1 atm, in kcal/mol

No.	Compound	$-\Delta H_c^0$ exp.	$-\Delta H_c^0$ calc.	$-\Delta H_f^0$
1	1,1-Dimethyl-2-ethylcyclopropane $C_7H_{14}$	1115.0	—	21.6
2	1,1-Dimethyl-2-propylcyclopropane $C_8H_{16}$	1271.2	1271.2	27.8
3	1,1-Dimethyl-2-butylcyclopropane $C_9H_{18}$	—	1427.4	33.9
4	1,1-Dimethyl-2-amylycyclopropane $C_{10}H_{20}$	—	1583.6	40.0
5	1,1-Dimethyl-2-hexylcyclopropane $C_{11}H_{22}$	1739.9	—	46.2

It is known that the presence in the molecule of cycloparaffins of an only slightly strained five-membered or six-membered ring practically does not affect the properties under consideration of the side chain (<sup>1</sup>). For the case of strained three- and four-membered rings, this question has until now remained unclarified. From the data obtained by us it follows that the presence of the cyclopropane ring is not reflected in the nature of the bonds in the substituent alkyl group, beginning already with ethyl. This conclusion, apparently, can also be extended to alkylcyclobutane compounds. Thus, the heats of combustion of compounds of the series of 1,1-dimethyl-2-*n*-alkylcyclopropanes (*n*-alkylethyl and other higher substituents) can be calculated from equation (3)

$$-\Delta H_c^0 = 1115.0 + (n - 7) 156.23, \quad (3)$$

where  $n \geq 7$  is the number of carbon atoms in the molecule.

In an analogous manner, the heats of formation can be calculated from equation (4):

$$-\Delta H_f^0 = 21.6 + (n - 7) 6.13. \quad (4)$$

From the heats of combustion of 1,1-dimethyl-2-ethyl-, 1,1-dimethyl-2-*n*-propyl-, and 1,1-dimethyl-2-*n*-hexylcyclopropanes and the literature values for  $A_{22}$  (156.231 kcal/mol) and  $A_{21}$  (263.238 kcal/mol), we calculated the increment  $c'$  entering into equations (1) and (2). The latter proved to be equal to  $c' = 851.74$  kcal/mol. The values of  $c'$ , calculated for  $-\Delta H_f'$ ,  $R_M$ , and  $V_M$ , are given in Table 2. It has now become possible to calculate the heats of combus-

...not only normal but also branched\* 1,1-dimethyl-2-alkylcyclopropanes. In this case equation (1) takes the form:

$$-\Delta H_c = 851.7 + \sum n_{ij} A_{ij} \quad \text{for } n \geq 7. \quad (5)$$

The values of the coefficients  $A_{ij}$  for C-C bonds of various subtypes in branched alkanes may be taken from the literature data (1).

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\* In the case of branching in the alkyl radical, beginning with the second carbon atom.

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

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