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Note

The enthalpies of combustion and formation of *cis*- and *trans*-1-methyl-1,2-dicyclopropylcyclopropane

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Abstract

Enthalpies of combustion of *cis*- and *trans*-1-methyl-1,2-dicyclopropylcyclopropane have been measured in a static bomb calorimeter. Enthalpies of formation have been derived for the isomers in the liquid and gaseous states.

INTRODUCTION

The present work is part of a programme of determination of the standard enthalpies of formation of cyclopropane derivatives.

EXPERIMENTAL

Materials

1-Methyl-1,2-dicyclopropylcyclopropane was prepared by the usual method from 5-methyl-3,5-dicyclopropylpyrasoline as a mixture of cis and trans isomers [1]. The isomers were separated chromatographically. The sample of *trans*-1-methyl-1,2-dicyclopropylcyclopropane contained 4.5 mol.% of the cis isomer, as was shown by chromatographic analysis. No impurities were found in the cis isomer.

Apparatus and procedure

The heat of combustion was determined using a static bomb calorimeter. The temperature rise was measured by a copper resistance thermometer ($R \approx 50\,\Omega$) and a bridge circuit [2]. The uncertainty of the temperature measurements was 4×10^{-5} K. The energy equivalent E of the calorimeter

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was determined by combustion of thermochemical standard benzoic acid with an energy of combustion of 26434.0 ± 2.2 J g^{-1} at 298.15 K. The value of the energy equivalent was equal to 50149.3 ± 5.0 J Ω^{-1}. Weighed amounts of the substances were sealed in glass ampoules and placed in a platinum crucible. The bomb with 1 cm^3 of added water was charged with purified oxygen to a pressure of 3.0 MPa. Provision for ignition was made using an iron wire heated by the discharge of the capacitor. After each run the combustion products were analysed for CO_2 by the Rossini method [3]. No soot was revealed after combustion experiments. Qualitative tests for CO with indicator tubes were negative within the limits of their sensitivity (0.0001 mol.%).

RESULTS AND DISCUSSION

Results of a typical combustion experiment for each isomer are given in Table 1. The symbols have the following meanings: m, sample mass; ΔR_{corr}, increase of thermometer resistance corrected for heat exchange; $E'\Delta R_{corr}$, the total energy change of the isothermal bomb process at 298.15 K (E' is the energy equivalent taken for the final state of the calorimetric system); $q(Fe)$, the heat of combustion of the iron wire; $q(HNO_3)$, the heat evolved in the formation of nitric acid; $\Delta_B U/M$, the specific energy of combustion at 298.15 K under the bomb conditions n, number of runs. The standard energies of combustion were obtained using the molar mass $M = 136.2364$ g mol^{-1} and the Washburn correction 2.5 kJ mol^{-1}.

The values of the standard energy of combustion $\Delta_c U°$ and enthalpy of combustion $\Delta_c H°$, together with the derived enthalpy of formation $\Delta_f H°$ for

TABLE 1

Typical combustion experiment data

Parameter [a]	Isomer	
	Cis	Trans
m/g	0.28482	0.26191
$\Delta R_{corr}/\Omega$	0.245806	0.225938
$E'\Delta R_{corr}/J$	13310.3	12234.7
$q(Fe)/J$	34.1	28.9
$q(HNO_3)/J$	6.5	2.6
Fraction of CO_2 found	0.9999	0.9999
$-\Delta_B U/M/(J\ g^{-1})$	46590	46593
$\langle -\Delta_B U/M \rangle/(J\ g^{-1})$	46599 ± 3 [b]	46583 ± 4 [b]
n	9	8

[a] See text for meaning of symbols.

[b] The standard deviation of the mean.

TABLE 2

Results and derived thermodynamic quantities at 298.15 K [a]

Isomer	$\Delta_c U^\circ(\mathrm{l})$/ kJ $\mathrm{mol^{-1}}$	$\Delta_c H^\circ(\mathrm{l})$/ kJ $\mathrm{mol^{-1}}$	$\Delta_f H^\circ(\mathrm{l})$/ kJ $\mathrm{mol^{-1}}$	$\Delta_v H^\circ$/ kJ $\mathrm{mol^{-1}}$	$\Delta_f H^\circ(\mathrm{g})$/ kJ $\mathrm{mol^{-1}}$
Cis	−6346.0 ± 1.1	−6355.9 ± 1.1	134.1 ± 1.2	46.9	181.0
Trans	−6343.8 ± 1.1	−6353.7 ± 1.1	131.9 ± 1.2	47.3	179.2

[a] See text for meaning of symbols.

the liquid and gaseous states are listed in Table 2. The following key $\Delta_f H^\circ$ values were used in the calculation: $\Delta_f H^\circ(\mathrm{CO_2, g}) = -393.51 \pm 0.13$ kJ $\mathrm{mol^{-1}}$ [4]; $\Delta_f H^\circ(\mathrm{H_2O, l}) = -285.830 \pm 0.040$ kJ $\mathrm{mol^{-1}}$ [4]. The enthalpy of vaporization $\Delta_v H^\circ$ was estimated according to the Klages equation [5].

The group contribution scheme of Benson et al. [6] gives 178.7 kJ $\mathrm{mol^{-1}}$ for enthalpies of formation of gaseous isomers, which is close to the experimental values. Apparently, no substantial stabilization or strain effect arise between three-membered rings bonded with a single C–C bond. The same conclusion has previously been reached for bicyclopropyl [7].

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