Thermochemical properties of polycyclic hydrocarbons including fragments of norbornane and small cycles

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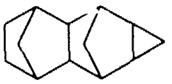
Combustion enthalpies of three polycyclic hydrocarbons were measured by the precision bomb calorimetry method and their enthalpies of formation in the liquid state were calculated: for pentacyclo[6.3.1.1^{3,6}.0^{2,7}.0^{9,11}]tridecene, −7713.9±3.8 and 25.8±3.8 kJ mol^{-1}; for 10-methylpentacyclo[6.3.1.1^{3,6}.0^{2,7}.0^{9,11}]tridecene, −8348.8±3.9 and −18.7±3.9 kJ mol^{-1}; and for 11-methylpentacyclo[6.4.1.1^{3,6}.0^{2,7}.0^{9,12}]tetradecene-10-spirocyclopropane, −10157.9±3.4 and 38.1±3.8 kJ mol^{-1}. The thermochemical parameters obtained agree with calculated values as well as with experimental and calculated enthalpies of formation of some hydrocarbons that contain the same fragments as the compounds studied.

Key words: calorimetry, enthalpies of combustion, enthalpies of formation, polycyclic hydrocarbons, thermochemical calculations.

Data on the thermodynamic parameters of compounds are necessary aids in the search for new efficient components of liquid fuel and lubricants. These components can be found among polycyclic hydrocarbons with complicated structures and high enthalpies of formation and densities.

The thermochemical properties of polycyclic compounds with norbornane fragments, which are of interest for both practical application and theoretical studies, have been poorly studied; there is only one paper on this subject,[1] in which the enthalpies of combustion and enthalpies of formation of tetracyclo[6.2.1.0^{2,7}.0^{3,5}]undecane, pentacyclo[6.3.1.0^{2,7}.0^{3,5}.0^{9,11}]dodecane, dispiro{cyclopropane-6,1′-pentacyclo[6.3.1.0^{2,7}.0^{3,5}.0^{9,11}]-dodecane-12,1′-cyclopropane} were experimentally determined.

In this work, the enthalpies of combustion ($\Delta_c H^o$) were determined and the enthalpies of formation ($\Delta_f H^o$) were calculated for three polycyclic hydrocarbons in the liquid phase: pentacyclo[6.3.1.1^{3,6}.0^{2,7}.0^{9,11}]tridecane, $C_{13}H_{18}$ (**1**); 10-methylpentacyclo[6.3.1.1^{3,6}.0^{2,7}.0^{9,11}]tridecane, $C_{14}H_{20}$ (**2**), and 11-methylpentacyclo[6.4.1.1^{3,6}.0^{2,7}.0^{9,12}]tetradecane-10-spirocyclopropane, $C_{17}H_{24}$ (**3**).



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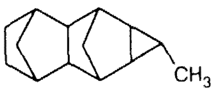

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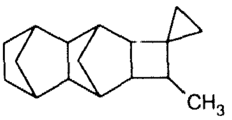

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Experimental

Compounds **1**—**3** were specially synthesized* for these thermochemical studies at the Institute of Organic Chemistry, RAS by a known procedure,[2] and they were chromatographically pure. Standard enthalpies of formation were determined by a method based on measuring the heat of combustion in a calorimetric bomb in excess oxygen. Heats of combustion were measured on two sealed semi-microcalorimeters, each equipped with an isothermal shell, a magnetic stirrer, and a calorimetric bomb, whose structural peculiarities were described in Refs. 3 and 4. The heat equivalents of the calorimeters were determined by the combustion of reference benzoic acid (K-1 trade mark) (the heat of combustion was −26434.93 J g^{-1}) and were equal to 6216.4 and 6449.5 J (rel. deg)$^{-1}$. The heat equivalents of the calorimeters obtained were checked by the combustion of a second reference compound, succinic acid. The studies performed and calibration of the instruments showed that in the calorimeters used it was possible to measure the heats of the combustion of reactions with an accuracy up to 0.02—0.03%, which is sufficient for studying energy-consuming polycyclic hydrocarbons. Procedures that take into account the specific features of combustion of energy-consuming hydrocarbons are described in detail in Refs. 4 and 5.

The initial pressure of oxygen for combustion of all compounds was 3.0 MPa. Water (1.0 mL) was injected into the

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calorimetric bomb prior to each experiment. The ignition was carried out by a dosed current pulse from a special device through a platinum wire.

The initial temperature of the calorimetric experiments was 298.15 K. Time was checked each 30 s. The initial, final, and main periods of a calorimetric experiment contained 20 readings. The constant of cooling of the calorimeter (0.00275) remained unchanged (within 1.5%) over a wide range of calorimeter temperatures.

The heats of combustion were measured for the following reactions:

$$C_{13}H_{18} + 17.5\,O_2 = 13\,CO_2 + 9\,H_2O, \qquad (1)$$

$$C_{14}H_{20} + 19\,O_2 = 14\,CO_2 + 10\,H_2O, \qquad (2)$$

$$C_{17}H_{24} + 23\,O_2 = 17\,CO_2 + 12\,H_2O. \qquad (3)$$

When the enthalpy of combustion was calculated according to standard procedures,[5,6] corrections for the heat effect of the formation of HNO_3 and the heat exchange between the calorimetric vessel and the shell, the Washbern correction, and other corrections necessary for precise calorimetric measurements, were introduced.

The enthalpies of formation of the compounds studied were calculated from the equations characterizing combustion in oxygen using the enthalpies of formation of CO_2(g) (−393.51±0.13 kJ mol^{-1}) and H_2O(liq) (−285.830±0.040 kJ mol^{-1}).[7]

Data from the series of experiments to determine the specific heat of combustion of the energy-consuming polycyclic hydrocarbons studied are presented in Tables 1—3.

The thermochemical properties of all hydrocarbons studied in this work are presented in Table 4.

Table 1. Heats of combustion of pentacyclo-[6.3.1.1^{3,6}.0^{2,7}.0^{9,11}]tridecane

Δm	ΔR	δ	q_{fil}	q_{HNO_3}	$\Delta_B U'$
0.107765	0.7601	0.0165	38.74	5.19	44242.5
0.109795	0.7713	0.0165	26.11	4.60	44190.8
0.109295	0.7711	0.0174	38.74	5.19	44252.5
0.103685	0.7281	0.0142	21.21	4.60	44204.3
0.110305	0.7756	0.0165	30.42	4.60	44194.0
0.110695	0.7790	0.0168	32.17	5.77	44206.5

$\Delta_B \bar{U}'$ = 44215.1±21.7 J g^{-1},
$\Delta_c H^\circ$ (liq) = 7713.9±3.8 kJ mol^{-1},
$\Delta_f H^\circ$ (liq) = 25.8±3.8 kJ mol^{-1}.

Note. Δm is the weight of a sample of a substance (g); ΔR is the corrected temperature increase in the calorimetric experiment (rel. deg); δ is the correction for heat transfer between the calorimetric vessel and the shell calculated by the Regnault—Pfaundler—Usov equation (rel. deg); q_{fil} is the heat effect of combustion of the incendiary filament (J); q_{HNO_3} is the heat effect of formation of nitric acid (J); $\Delta_B U'$ is the specific heat of combustion of the compound studied under the calorimetric bomb conditions (J g^{-1}); $\Delta_B \bar{U}'$ is the average specific heat of combustion of the compound studied (kJ mol^{-1}); $\Delta_c H^\circ$ is the standard heat of combustion of the compound studied (kJ mol^{-1}); $\Delta_f H^\circ$ is the standard enthalpy of formation of the compound (kJ mol^{-1}).

Table 2. Heats of combustion of 10-methylpentacyclo[6.3.1.1^{3,6}.0^{2,7}.0^{9,11}]tridecane

Δm	ΔR	δ	q_{fil}	q_{HNO_3}	$\Delta_B U'$
0.102515	0.7242	0.0147	38.91	5.77	44283.9
0.105645	0.7449	0.0163	30.12	5.77	44295.5
0.105415	0.7438	0.0159	34.85	5.77	44286.9
0.105175	0.7414	0.0139	32.35	4.60	44270.2
0.105945	0.7471	0.0152	27.32	5.19	44333.6
0.105995	0.7463	0.0165	23.89	5.19	44297.2
0.110075	0.7757	0.0163	36.65	5.77	44224.9
0.107605	0.7587	0.0159	29.37	5.77	44307.5

$\Delta_B \bar{U}'$ = 44287.5±21.0 J g^{-1},
$\Delta_c H^\circ$ (liq) = 8348.8±3.9 kJ mol^{-1-1},
$\Delta_f H^\circ$ (liq) = −18.7±3.9 kJ mol^{-1-1}.

Table 3. Heats of combustion of 11-methylpentacyclo[6.4.1.1^{3,6}.0^{2,7}.0^{9,12}]tetradecane-10-spirocyclopropane

Δm	ΔR	δ	q_{HNO_3}	$\Delta_B U'$
0.105605	4.51288	0.12424	6.95	44427.8
0.061735	2.63765	0.04345	4.35	44414.4
0.099440	4.24993	0.11299	6.65	44432.0
0.100490	4.29313	0.11428	6.65	44415.3
0.099570	4.25660	0.11135	6.65	44443.7
0.088130	3.60366	0.06285	5.19	44443.7
0.107045	4.37331	0.09872	5.77	44410.2
0.095495	3.90764	0.08077	5.77	44474.2

$\Delta_B \bar{U}'$ = 44432.8±15.9 J g^{-1},
$\Delta_c H^\circ$ (liq) = 10157.9±3.4 kJ mol^{-1},
$\Delta_f H^\circ$ (liq) = 38.1±3.8 kJ mol^{-1}.

Table 4. Thermochemical properties of hydrocarbons studied

Compound	$\Delta_B \bar{U}'$ /J g^{-1}	$\Delta_c H^\circ$(l) /kJ mol^{-1}	$\Delta_f H^\circ$(l) /kJ mol^{-1}
1	44215.1±21.7	7713.9±3.8	25.8±3.8
2	44287.5±21.0	8348.8±3.9	−18.7±3.9
3	44432.8±15.9	10157.9±3.4	38.1±3.8

Results and Discussion

The thermochemical parameters obtained make it possible to develop a method for calculating the thermochemical properties of complicated polycyclic hydrocarbons.

The classification of molecular fragments by groups of atoms is used as a basis for the calculation scheme.[8—10] The scheme contains a system of group contributions, which is substantially extended by new fragments and takes into account interactions of functional groups with each other. This makes it possible to calculate the properties of broad classes of organic compounds with complicated structures. The values of the parameters of acyclic

Table 5. Comparison of experimental and calculated enthalpies of formation of polycyclic hydrocarbons in the liquid state

Hydrocarbon		$\Delta_f H^o$(l)		$\Delta\Delta H$*	Ref.
		experiment	calculation		
Methylcyclopropane		−1.7	5.6	−5.3	10
Cyclobutane		−3.7	5.1	−8.8	10
Methylcyclobutane		44.5	34.7	9.8	10
Cyclopentane		105.1	107.4	−2.3	10
Cyclohexane		156.4	157.2	−1.2	10
Bicyclo[3.1.0]hexane		−5.1	2.2	−2.8	10
Bicyclo[2.2.1]heptane		102.1	99.7	2.4	10
Bicyclo[4.1.0]heptane		36.7	35.4	1.3	10
Bicyclo[4.2.0]octane		68.1	72.8	−4.7	10
Methylbicyclo[2.2.1]heptane					
	exo	122.5	129.3	6.8	10
	endo	122.1	129.3	7.2	10
Dimethylbicyclo[2.2.1]heptane					
	trans	150.2	159.0	8.8	11
Bicyclo[4.3.0]nonane					
	cis	173.1	175.1	−2.0	10
	trans	176.2	175.1	1.1	10
Decalin	*cis*	219.4	225.3	−5.9	10
	trans	230.6	225.3	5.3	10
Methyldecalin	*cis*	243.8	242.3	1.5	10
	trans	249.7	242.3	7.4	10
1-Methylbicyclo[2.2.1]heptane		131.0	135.0	−4.0	10
2,3-Dimethylbicyclo[2.2.1]-heptane		150.2	159.0	−8.8	10
Tetracyclo[6.2.1.$0^{2,7}$.$0^{3,5}$]-undecane		3.8	−1.3	5.1	9
1		25.8	15.1	10.9	**
2		−18.7	−14.8	−3.9	**
3		38.1	37.7	0.4	**

* $\Delta\Delta H = \Delta_f H^o_{exp}(liq) - \Delta_f H^o_{calc}(liq)$.

** This work.

segments of a molecule and the corrections for the cycles, which are necessary for calculating entropies of formation in the liquid state, were taken from Refs. 8—10. These parameters were determined by optimization of the data from a set of selected reliable thermochemical parameters for more than 300 organic compounds of various classes.

New parameters, which make it possible to calculate the properties of hydrocarbons containing fused norbornane fragments, were obtained from the enthalpies of formation of the compounds studied in this work and from the data in Ref. 11 and in handbooks.[11—13]

The experimental thermochemical parameters obtained are compared with the calculated values and with the experimental and calculated enthalpies of formation of some hydrocarbons containing the same fragments as the compounds studied (Table 5).

The data in Table 5 show that the calculation accuracy for both bicyclic and polycyclic hydrocarbons is equal to 4—6 kJ mol^{-1} on average, which is comparable with the accuracy of the experimental determination of enthalpies of combustion and formation of complicated hydrocarbons. The enthalpies of formation of the compounds studied agree satisfactorily with each other and with the published data for other hydrocarbons, which confirms their reliability.

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