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Enthalpy of Formation of 2,2,6,6-Tetramethyl-4-heptanone

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The enthalpies of combustion and vaporization have been measured for 2,2,6,6-tetramethyl-4-heptanone. The following enthalpies of formation at 25.0°C have been derived:

$\Delta H^\circ_f(l) = -474.1 \pm 3.5$ kJ mol^{-1}

$\Delta H^\circ_f(g) = -421.2 \pm 3.5$ kJ mol^{-1}

A comparison of the result with a value calculated from a previously derived equation indicates that the molecule is free from any destabilising steric effects.

In a previous paper,[1] enthalpies of formation of several aliphatic branched ketones were reported. An equation was presented correlating enthalpy of formation data for sixteen ketones and showing that 2,2,4,4-tetramethyl-3-pentanone was destabilised by steric effects by about 20 kJ mol^{-1}. No such effects were found in 2,2,5,5-tetramethyl-3-hexanone. The object of the present study was to see if the equation given in Ref. 1 would be valid for the corresponding tetramethyl-4-heptanone in which steric effects would be expected to be absent.

EXPERIMENTAL

Compounds. 2,2,6,6-Tetramethyl-4-heptanone was synthesized by Drs. Lennart Eberson and Klas Nyberg, Dept. of Organic Chemistry, Chemical Center, Lund. The impure synthesis product was purified by preparative gas chromatography (Perkin-Elmer F 21) on a 4.5 m 20 % Carbowax 20M on Chromosorb A column. The purification process proved difficult, and only by injecting 50 μl samples could the pure compound be obtained. The purity was checked using GLC on Apiezon L and Carbowax 20M columns, which showed the absence of organic impurities. The substance was dried with molecular sieves 4A.

The water content of the sample was determined using a gas chromatographic method [2] and found to be 0.002 vol. %.

The density of the pure compound was 0.8071 g ml^{-1} at 25°C.

Combustion calorimetry – apparatus and procedure. A rotating-bomb calorimeter, TKL-2, with internal bomb volume 0.2622 dm^3, was used for the measurements. Details of the calorimetric procedure have been given previously [3] with one major difference. The platinum resistance thermometer and bridge measuring system were replaced by a Hewlett Packard HP-2801A Quartz Thermometer with a 2850D probe. The thermometer was used in the 100 sec range with a resolution of 0.00001°C in conjunction with a digital recorder. Fore-, main-, and after-periods were all of 20 min duration.

Table 1. Results of combustion experiments.

ε°(Calor) = 28 167.0 ± 2.3 J K^{-1}; $(\Delta U_c^{\circ}/M)$(oil) = −(45.9459 ± 0.0042) kJ g^{-1};
m(Pt) = 11.915 g; $(\Delta U_c^{\circ}/M)$(fuse) = −(16.807 ± 0.004) kJ g^{-1}.

m'(comp.)/g	m''(oil)/g	m'''(fuse)/g	$\Delta\theta$/K	m^i(cont.)/g	ε^i(cont.)/J K^{-1}	$\Delta U^f_{dec}(HNO_3)$/J	$\Delta U\Sigma$/J	$[-\Delta U_c^{\circ}/M$(comp.)]/J g^{-1}
0.247205	0.232812	0.001206	0.743333	23.631	13.56	8.09	6.61	41028.3
0.301259	0.185786	0.001444	0.745500	23.653	13.55	6.37	6.73	41032.6
0.301276	0.183398	0.001378	0.741367	23.637	13.54	6.65	6.68	41012.2
0.302667	0.182563	0.001392	0.742225	23.642	13.54	7.25	6.68	41026.5
0.300424	0.185820	0.001411	0.744183	23.636	13.54	6.18	6.72	41021.0

Mean $-\Delta U^{\circ}_c/M = 41024.1 \pm 3.5$ J g^{-1}

Since very little of the pure substance was available, the amount of substance used in each combustion corresponded to between 49 and 60 % of the total heat evolved in the bomb process. The sample was transferred under vacuum from the molecular sieves to a receiver containing the soda-glass ampoules, to be filled for the combustion experiments and water determination. The mass of the ampoules was about 50 mg.

All weighings were reduced to mass, and the molecular weights were computed from the 1969 table of atomic weights.[4]

Vaporization calorimetry. The enthalpy of vaporization at 25°C for the compound was measured using the Wadsö calorimeter.[5]

RESULTS

The results are expressed in terms of absolute joules. Symbols and calculational procedure used were as previously,[1] with the exception that the Washburn corrections, ΔU_Σ, were computed on a Univac 1108. The values used for the specific heat capacity, C_p, and $(\delta V/\delta T)_p$, were 1.67 J K^{-1} g^{-1} and 1.42 mm^3 K^{-1} g^{-1}, respectively.

The final over-all precision of the ΔU_c° mean values was estimated as given in Ref. 3. Enthalpies of formation at 25°C for gaseous CO_2 and liquid water were taken from Ref. 6. The results from the combustion experiments are shown in Table 1. The ΔU_c° values refer to the idealized combustion reaction, in which all reactants and products are in their thermodynamic standard states at 25°C.

Table 2. Results and derived quantities at 25°C.

ΔU_c°/kJ mol^{-1}	-6986.28 ± 2.23
ΔH_c°/kJ mol^{-1}	-6998.62 ± 2.23
ΔH_f°(l)/kJ mol^{-1}	-474.1 ± 3.5
ΔH_v/kJ mol^{-1}	52.9 ± 0.2
ΔH_f°(g)/kJ mol^{-1}	-421.2 ± 3.5

Table 2 gives the standard energy, ΔU_c°, and enthalpy, ΔH_c°, of combustion together with the enthalpy of vaporization, ΔH_v, and derived enthalpies of formation, ΔH_f°, for the liquid and gaseous states at 25.0°C. The uncertainties given are twice the final over-all standard deviation of the mean.*

DISCUSSION

The enthalpy of formation of 2,2,6,6-tetramethyl-4-heptanone may be calculated from the equation given in Ref. 1 using the values $n=11$, $b_3=15$, $c_4=8$, and $c_4'=0$. The value obtained is $\Delta H_f^\circ(g) = -422.0$ kJ mol^{-1}. The enthalpy of formation derived experimentally, -421.2 ± 3.5 kJ mol^{-1}, is in excellent agreement with this calculated value. Since the equation used takes no account of destabilisation due to steric hindrance, this indicates that 2,2,6,6-tetramethyl-4-heptanone is free from any such effects, which is in accordance with the results for the corresponding tetramethyl-3-hexanone.[1]

* After this work was completed an uncertainty arose in the value for the energy of combustion of the paraffin oil, and the uncertainties associated with the enthalpy of formation values have been correspondingly increased.

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REFERENCES

1. Sellers, P. *J. Chem. Thermodynamics* **2** (1970) 211.
2. Sellers, P. *Acta Chem. Scand.* **25** (1971) 2295.
3. Månsson, M. *J. Chem. Thermodynamics* **1** (1969) 141.
4. *Compt. Rend. XXVth IUPAC Conference* 1969, 103.
5. Wadsö, I. *Acta Chem. Scand.* **20** (1966) 536.
6. *Selected Values of Chemical Thermodynamic Properties*, National Bureau of Standards, Technical Note 270–3, January 1968.

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