Enthalpies of Formation of *cis*- and *trans*-8-Methyl-2-hydrindanone

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Enthalpies of combustion and vaporization/sublimation have been measured for *cis*- and *trans*-8-methyl-2-hydrindanone. The following enthalpies of formation at 25.0°C have been derived:

	ΔH_f°/kJ mol^{-1}
cis-8-methyl-2-hydrindanone (c)	-347.9 ± 3.4
cis-8-methyl-2-hydrindanone (g)	-287.0 ± 3.4
trans-8-methyl-2-hydrindanone (l)	-333.5 ± 2.2
trans-8-methyl-2-hydrindanone (g)	-275.2 ± 2.3

The *cis*-isomer was found to be more stable at 25°C to the extent of 11.8 ± 3.8 kJ mol^{-1}. This result is discussed in relation to other isomer pairs of the hydrindane system.

Hydrindane is a system in which a six-membered ring is joined to a five-membered ring in the 1,2-position. The rings can be connected in a *cis*- or *trans*-arrangement, the *cis*-form requiring an *equatorial* and an *axial* bond, and the *trans*-form two *equatorial* bonds. This ring system exists in many natural products, steroids for example, whose stereochemistry usually can be related to that of the simple system and this confers a special interest to the conformations and relative stabilities of hydrindane and its derivatives. Predictions of relative stabilities in such systems, especially when substituents or functional groups are introduced, are difficult to make. This work describes the determination of the enthalpies of formation of the *cis*- and *trans*-isomers with both an angular methyl substituent and a ketone function introduced into the ring system.

EXPERIMENTAL

Compounds *

trans-10-Methyl-decalin-2-one. Following the procedure of Stork and Darling,[1] 21 g (0.13 mol) 10-methyl-$\Delta^{1(9)}$-octalin-2-one was reduced with 8.95 g (1.3 mol) of lithium in 600 ml of dry ammonia. The crude product was fractionally distilled twice through an 18″ spinning band column, b.p. 128—130°C (20 mmHg), yield 13.1 g (62 %).

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* The synthetic work was performed at University of California, Berkeley, by W. G. Dauben, D. Murphy and W. T. Wipke.

This reaction was repeated eight times, the products combined, and redistilled. The purity of the material was determined by GLC analysis at 140°C using a 100′ capillary column coated with Apiezon L; the material contained 96 % of the *trans*- and 4% of the *cis*-isomer.

trans-1-*Methylcyclohexane-1,2-diacetic acid.* To a vigorously stirred suspension of 0.3 g of vanadium pentoxide in 230 ml of refluxing concentrated nitric acid there was slowly added over a period of 10 min 23.5 g of 96 % pure *trans*-ketone prepared above. The dark red solution was heated under reflux for 5 min, 100 ml of water added, and the heating continued for 1 h. The solution was cooled for 12 h, the white solid filtered ,and the material recrystallized three times from 50 % aqueous acetic acid, yield 12 g (38 %), m.p. 195.5−196.5°C (lit.[1,2] 197.4−198.8°C).

This reaction was repeated four times, and the acid combined and recrystallized, m.p. 195−196°C.

trans-8-*Methyl-2-hydrindanone.* A mixture of 50.5 g (0.236 mol) of the *trans*-diacid (prepared above) and 4.0 g of barium hydroxide was pyrolyzed under nitrogen at a temperature of 315−330°C. The cloudy distillate was dissolved in 150 ml of ether and the ethereal solution was washed with 10 % sodium hydroxide solution and saturated salt solution. The solution was dried, the solvent removed and the crude ketone distilled through an 18″ spinning band column, b.p. 109−110°C(10 mmHg), yield 20.8 g (58 %), n_D^{25} 1.4784 [lit.[2] b.p. 109−110°C (20 mmHg), n_D^{25} 1.4794]. GLC analysis at 100° on a 150′ capillary column coated with Apiezon L showed no detectable impurities.

cis-10-*Methyldecalin-2-one.* A solution of 100 g (0.61 mol) of 10-methyl-$\Delta^{1(9)}$-octalin-2-one in 200 ml of absolute methanol was hydrogenated for 2 h over 1.5 g of 10 % palladium on strontium carbonate catalyst. The mixture was filtered, the solvent removed under reduced pressure, and the waxy solid recrystallized three times from petroleum ether (−40°C), yield 68 g (68 %), m.p. 48.4−49.6°C (lit.[3] m.p. 46−48°C).

This reaction was repeated, the products combined, and recrystallized. GLC analysis using the conditions described for the *trans*-isomer showed that the material was 99 % *cis* and 1 % *trans*.

cis-1-*Methylcyclohexane-1,2-diacetic acid.* Following the procedure used for the *trans*-isomer, 30 g (0.18 mol) of the 99 % pure *cis*-ketone was oxidized and the resulting acid recrystallized three times from 50 % aqueous acetic acid; yield 17.8 g (47 %), m.p. 191−192°C (lit.[2] m.p. 191.2−192.9°C).

This reaction was repeated, the acids combined, and recrystallized, m.p. 191.5−192.5°C.

cis-8-*Methyl-2-hydrindanone.* Following the procedure used for the *trans*-isomer, 33 g (0.15 mol) of the *cis*-diacid yielded 23 g of a waxy solid which was distilled, b.p. 54−56°C (0.8 mmHg) yield 13 g (57 %). The material solidified at room temperature and a small sample was recrystallized from petroleum ether, m.p. 37.1−37.9°C (lit.[4] m.p. 40°C). GLC analysis, as for the *trans*-isomer, showed no detectable impurities. However, further GLC studies using a column of 5 % Carbowax 1500 on 60−80 mesh Chromosorb G, at 50° (Pye Argon Gas Chromatograph) indicated the presence of approximately 0.06 mol% impurity. From the synthesis route and from the retention times it was deduced that the impurity was the isomeric *cis*- or *trans*-1-hydrindanone and such small amounts of isomer will not significantly affect the enthalpy of combustion results.

Combustion calorimetry − Apparatus and procedure

Two rotating-bomb calorimeter systems were used, TKL-2 with internal bomb volume 0.2634 dm³ for the *trans*-isomer, and TKL-3 with internal bomb volume 0.2613 dm³ for the *cis*-compound. Details of the calorimetric procedure have been given previously.[5]

trans-8-*Methyl-2-hydrindanone.* The substance was treated with calcium hydride under vacuum for 24 h and then transferred to a receiver containing the evacuated soft-glass ampoules to be filled for the combustion experiments.[6] Eight filled ampoules were obtained, seven being used for combustion measurements and one for determination of the water content of the sample using a method based on reaction with CaH_2 and volumetric determination of the evolved hydrogen. The water content was found to be less than ±0.006 mass per cent and was considered to be negligible.

cis-8-Methyl-2-hydrindanone. Since the substance was crystalline at room temperature the glass ampoule technique could not be used. Instead, the sample was enclosed in polyester bags made from Du Pont's 100 gauge Mylar Type A, using the technique described by Good *et al.*[7] The substance was dried by stirring with Molecular Sieves 5A for several hours, at a temperature of about 45°C. The substance was then sublimed off from the sieves under vacuum. Each Mylar bag, pre-weighed at known relative humidity, was filled with substance and sealed in a dry-box to prevent uptake of moisture by the substance, and then put into another Mylar bag which was also sealed in the dry-box.

Initial combustion experiments with about 0.5 g substance gave rise to large quantities of soot. Attempts to overcome this difficulty by pressing the bags and substance into the form of a pellet, and thus removing occluded gases, were unsuccessful, soot being formed as before. It was found necessary to reduce the quantity of substance used to an amount corresponding to between 48 and 67 % of the total heat evolved in a combustion experiment, and using paraffin oil as auxiliary combustion material.

All weighings were reduced to mass and the molecular weights computed from the 1961 table of atomic weights.[8] The density of the *trans*-isomer was 0.98 and that of the *cis*-isomer 1.03 g ml^{-1}.

Vaporization calorimetry

The enthalpy of vaporization of the *trans*-isomer and the enthalpy of sublimation of the *cis*-isomer at 25.0°C were measured in the calorimeter described by Morawetz.[9]

RESULTS

The results are expressed in terms of absolute joules. The symbols used are those of Hubbard, Scott and Waddington [10] except that internal energy is now represented by U. The Washburn corrections, ΔU_{Σ}, were calculated using SMIL, electronic computer of the University of Lund, with a modified version of the calculational procedure given in Ref. 10. The values used for the specific heat capacity, C_p, and $(\delta V/\delta T)_p$ were 2.09 J K^{-1}g^{-1} and 0.774 mm^3 K^{-1}g^{-1} for the *trans*-isomer and 1.38 J K^{-1}g^{-1} and 0.388 mm^3 K^{-1}g^{-1} for the *cis*-isomer, respectively.

The final over-all precision of the ΔU_c° mean values was estimated as given in Ref. 5. Enthalpies of formation at 25.0°C for gaseous CO_2 and liquid water have been taken from Ref. 11 with 1 cal = 4.184 J. Data for a typical combustion experiment for each compound are given in Table 1. The results from the different series of measurements are summarized in Table 2. The ΔU_c° values refer to the idealized combustion reaction in which all reactants and products are in their thermodynamic standard states at 25.0°C.

Table 3 gives the standard energies, ΔU_c°, and enthalpies, ΔH_c°, of combustion together with the enthalpies of vaporization and sublimation, $\Delta H_{vap.}$ and $\Delta H_{subl.}$, and derived enthalpies of formation, ΔH_f°, for the liquid or solid and gaseous states at 25.0°C.

DISCUSSION

From the results presented in Table 3 the *cis*-isomer is found to be the more thermochemically stable at 25°C by 11.8 ± 3.8 kJ mol^{-1}. This is the most usual situation between *cis*- and *trans*-isomers of the hydrindane system, but two notable exceptions are the parent hydrindane and the 2-hydrindanone without the angular methyl substituent. The relative stabilities of the *cis*-

Table 1. Summary of typical combustion experiments.

$(\Delta U_c^\circ/M)(\text{Mylar}) = -[(22.8969 - 0.0011 \cdot \text{RH}) \pm 0.0033] \text{ kJ g}^{-1}$
$(\Delta U_c^\circ/M)(\text{Oil}) = -(45.9587 \pm 0.0038) \text{ kJ g}^{-1}$
$(\Delta U_c^\circ/M)(\text{Fuse}) = -(16.807 \pm 0.004) \text{ kJ g}^{-1}$

	trans-8-Methyl-2-hydrindanone	*cis*-8-Methyl-2-hydrindanone
Calorimeter	TKL-2	TKL-3
m'(comp.)/g	0.466 709	0.359 927
m''(oil)/g	0.064 890	0.127 231
m'''(fuse)/g	0.001 549	0.001 600
m(Mylar)/g	—	0.048 463 (RH=51)
m(Pt)/g	10.125	20.538
$\Delta\theta$/K	0.741 980	0.739 373
ε°(calor)/J K^{-1}	28 436.7	28 330.2
m^i(cont.)/g	22.015	32.203
ε^i(cont.)/J K^{-1}	13.60	14.60
$\Delta U_{\text{dec}}{}^f$(HNO$_3$)/J	3.10	4.14
ΔU_Σ/J	8.33	8.62
$[\Delta U_c^\circ/M(\text{comp.})]$ J g^{-1}	38 614.2	38 518.9

Table 2. Results of combustion experiments at 25.0°C.
$$-(\Delta U_c^\circ/M) \text{ kJ g}^{-1}$$

	trans-8-Methyl-2-hydrindanone	*cis*-8-Methyl-2-hydrindanone
	38.627 9	38.545 3
	38.614 2	38.518 9
	38.628 0	38.515 8
	38.628 1	38.517 3
	38.608 9	38.535 2
	38.601 8	
	38.637 8	
Mean	38.620 9	38.526 5
Standard deviation	0.004 9	0.005 9

Table 3. Results and derived quantities at 2.50°C.

	ΔU_c°/kJ mol^{-1}	ΔH_c°/kJ mol^{-1}	ΔH_f°(1 or c)/ kJ mol^{-1}	ΔH(vap.or subl.)/kJ mol^{-1}	ΔH_f°(g)/kJ mol^{-1}
trans-8-Methyl-2-hydrindanone	-5879.57 ± 2.18	-5888.23 ± 2.18	-333.51 ± 2.22	58.32 ± 0.17	-275.19 ± 2.26
cis-8-Methyl-2-hydrindanone	-5865.17 ± 3.35	-5873.83 ± 3.35	-347.90 ± 3.38	60.92 ± 0.17	-286.98 ± 3.43

The uncertainties given are twice the final overall standard deviation of the mean.

and *trans*-isomers of hydrindane have been determined by combustion calo-
rimetry to be 4.4 ± 2.2 kJ mol^{-1} for the vapour state and 3.1 ± 2.2 kJ mol^{-1}
for the liquid state,[12] with the *trans*-isomer the more stable. Similar values
have been obtained from equilibrium studies on the two isomers.[13,14] The
cis-isomer has a higher entropy than the *trans* [13,14] and this combined with
the low enthalpy difference leads to a change in the stability conditions at
higher temperatures, and above 193°C the *cis*-isomer predominates.[13] Since
ΔG at 25°C is small (about 1 kJ mol^{-1} in favour of the *trans*-isomer) minor
changes in structure, such as the introduction of an angular methyl group,
the introduction of a ketone function in various parts of the ring system, or
the partial locking of the *cis*-hydrindane system in a steroid, often are sufficient
to nullify stability considerations based on the parent isomers. Consequently,
predictions in such systems are difficult. Few thermodynamic data are avail-
able but it has been shown that *cis*-1-hydrindanone [15] and *cis*-4-hydrindanone [16]
predominate over the *trans*-isomers at equilibrium, and *trans*-2-hydrindanone
is thermochemically more stable at 25°C than its *cis*-isomer based on enthalpy
of combustion measurements.[17] The value given in Ref. 17 for the enthalpy
of isomerization *trans*-2-hydrindanone → *cis*-2-hydrindanone is 18.0 kJ mol^{-1}
but another value also given by Hückel [18] is 8.4 kJ mol^{-1}. These values are not
corrected to modern energy units and refer to the liquid state. Values for the
enthalpies of formation in the vapour phase, the correct reference state, are
not known and might change the stability situation considerably. Since the
combustion work is so unreliable a new determination of the enthalpies of
formation of these isomers is being carried out in this laboratory.

No thermochemical data are available for any compounds of the 8-methyl
hydrindane series but it has been indicated [19] that the *cis*-isomer should in
general be the more stable. From model studies on the 8-methyl hydrindanes
it may be seen that the *trans*-isomer contains one more *gauche* interaction than
the *cis*-isomer which should make the latter more stable by about 3.5 kJ mol^{-1}.
Allinger *et al.*[20] have calculated the enthalpies of formation of these isomers
using the Westheimer method and predict that the *cis* compound should be
more stable to the extent of about 2.8 kJ mol^{-1}. Their results for a wide range
of cyclic and bicyclic hydrocarbons are usually in good agreement with experi-
mental values so that their prediction should be reliable and fits in with the
other [19] available evidence. The value found here for the enthalpy of isomeriza-
tion *cis*-8-methyl-2-hydrindanone → *trans*-8-methyl-2-hydrindanone, 11.8 kJ
mol^{-1}, is surprisingly high, especially when considering the situation in 2-
hydrindanones with no angular methyl substituent. Clearly, some other
factor than *gauche* interactions is in operation here, probably strain in the
different ring systems. An extension of the Westheimer calculation method
to non-hydrocarbons giving both enthalpies of formation and minimum
energy conformations would be of value in elucidating the reason for the
relatively large differences in stability in 2-hydrindanone systems.

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