

Enthalpies of Formation of *cis*- and *trans*-2-Hydrindanone

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Enthalpies of combustion and vaporization have been measured for *cis*- and *trans*-2-hydrindanone. The following enthalpies of formation at 25°C have been derived:

	$\Delta H_f^\circ(l)/\text{kJ mol}^{-1}$	$\Delta H_f^\circ(g)/\text{kJ mol}^{-1}$
<i>cis</i> -2-hydrindanone	-307.1 ± 1.3	-249.6 ± 1.3
<i>trans</i> -2-hydrindanone	-305.3 ± 1.6	-249.2 ± 1.6

The isomers were found to be of the same thermochemical stability within the limits of errors. The result, supported by conformational calculations, is compared to previous data and discussed in relation to compounds of similar type.

In a previous paper¹ results were presented for the enthalpies of formation of *cis*- and *trans*-8-methyl-2-hydrindanone, and the relative stabilities of the isomers were discussed. The *cis*-isomer was shown to be the more stable one at 25°C, in contrast to the reported situation² with the isomer pair without the angular methyl group. These latter data were not considered particularly reliable, and referred only to the liquid state, so that a redetermination of the enthalpies of combustion combined with enthalpy of vaporization measurements was judged to be necessary to clarify the situation. In addition, preliminary results were now available from conformational calculations on some hydrindane systems, with and without angular methyl substituents, which could be compared with the experimental data.

EXPERIMENTAL

Compounds. *trans*-2-Hydrindanone. This isomer was prepared following in general the method given by Hückel and Friedrich.² *trans*-2-Decalol (Koch-Light Ltd.) was converted *via trans*- Δ_2 -octalin to *trans*-cyclohexane-1,2-diacetic acid. The acid was then distilled with acetic anhydride to give the *trans*-2-hydrindanone in 55 % yield.

The crude product from the synthesis was purified on a spinning-band distillation column (Nester-Faust) under reduced pressure (main fraction: b.p. 115°C at 45 mm Hg). The purity of the sample was then checked by GLC on Carbowax 20M and NPGS columns. The only organic impurity which could be detected was the *cis*-isomer in amounts less than 0.05 %. No accurate quantitative determination of this amount could be made, but, since it was so low and would not significantly affect the combustion results, no correction was applied for this impurity.

The substance was dried by shaking with molecular sieves, 4A. The water content of the sample was determined on ampoules (filled at the same time as for combustion experiments) using a gas chromatographic method.³ The result was 0.003 vol.%, and, again, no correction was applied to the combustion results for this amount.

The density of the pure material at 25°C was 0.9791 g ml⁻¹.

cis-2-Hydrindanone. This isomer was prepared starting from *cis*-hexahydrophthalic anhydride, which was first converted to the corresponding diethyl phthalate.⁴ The ester was converted to *cis*-cyclohexane-1,2-diacetic acid *via* the corresponding alcohol,⁵ tosylate,⁶ and cyanide.⁶ The diacid was then pyrolysed with BaO⁷ to give the desired ketone in good yield.

The purity of the product was checked by GLC in the same way as for the *trans*-isomer. The only impurity detected was the *trans*-isomer. The amount of this impurity was determined from the areas of the respective peaks on the gas chromatogram, assuming that the detector response (FID) was the same for both isomers. The amount of *trans*-isomer was determined to be 10.7 ± 0.2 mol%.

After drying with molecular sieves, the water content of the sample was determined as for the *trans*-isomer and found to be 0.01 wt. %.

The density of the sample at 25°C was 0.9968 g ml⁻¹.

Combustion calorimetry—apparatus and procedure. The apparatus and calorimetric procedure were as described previously.^{8,9} The samples were transferred under vacuum from the molecular sieves to a receiver containing the soda-glass ampoules to be filled for the combustion experiments and water content determination. The mass of the ampoules was about 60 mg.

All weighings were reduced to mass, and the molecular weights computed from the 1969 Table of Atomic Weights.¹⁰

Vaporization calorimetry. The enthalpy of vaporization of the *trans*-isomer was determined using the calorimeter described by Morawetz,¹¹ and that of the *cis*-isomer, using the Wadsö calorimeter.¹²

RESULTS

The results are expressed in terms of absolute joules. The symbols and calculational procedure used were as before.^{8,9} The value used for the specific heat capacity, C_p , of both isomers was 1.67 J K⁻¹g⁻¹. Values of $(\partial V/\partial T)_p$ were calculated from measured densities at 20 and 25°C, and were 0.825 and 0.830 mm³ K⁻¹g⁻¹ for the *trans*- and *cis*-isomers, respectively.

Auxiliary data used and estimation of the final over-all precision were as previously.⁸ 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, where the uncertainties are standard deviations of the mean. The values of $\Delta U_c^\circ/M$ for the *cis*-isomer refer to the actual isomer mixture used in the combustion experiments, and the mean $\Delta U_c^\circ/M$ value given in Table 2 refers to the pure *cis*-isomer after correction for the presence of 10.7 % *trans*-isomer, and 0.01 wt. % water.

In Table 3 are presented the standard energies, ΔU_c° , and enthalpies, ΔH_c° , of combustion together with the enthalpies of vaporization, ΔH_v , and derived enthalpies of formation, ΔH_f° , for the liquid and gaseous states at 25°C. Uncertainties given are twice the over-all standard deviation of the mean.

DISCUSSION

Within the limits of error, the two isomers have the same enthalpy of formation in the vapour state, and are thus equally stable at 25°C, if stability is based on enthalpy data. Hückel has stated that the *trans*-isomer is the

Table 1. Summary of typical combustion experiments.

	$\varepsilon^\circ(\text{calor})$	$= (28167.0 \pm 2.3) \text{ J K}^{-1}$
	$(\Delta U_c^\circ/M)(\text{oil})$	$= -(45.9459 \pm 0.0042) \text{ kJ g}^{-1}$
	$(\Delta U_c^\circ/M)(\text{fuse})$	$= -(16.807 \pm 0.004) \text{ kJ g}^{-1}$
	<i>trans</i> -2-Hydrindanone	<i>cis</i> -2-Hydrindanone
$m'(\text{comp.})/\text{g}$	0.392628	0.444903
$m''(\text{oil})/\text{g}$	0.137603	0.083551
$m'''(\text{fuse})/\text{g}$	0.001448	0.001534
$m(\text{Pt})/\text{g}$	11.915	11.916
$\Delta\theta/\text{K}$	0.755552	0.737168
$m^1(\text{cont.})/\text{g}$	23.685	23.693
$\varepsilon^1(\text{cont.})/\text{J K}^{-1}$	13.59	13.56
$\Delta U_{\text{dec}}^1(\text{HNO}_3)/\text{J}$	7.09	0.94
$\Delta U\Sigma/\text{J}$	8.27	8.34
$[-\Delta U_c^\circ/M(\text{comp.})]/\text{J g}^{-1}$	37835.1	37821.6

Table 2. Results of combustion experiments at 25°C.

	$-(\Delta U_c^\circ/M) \text{ kJ g}^{-1}$	$-(\Delta U_c^\circ/M) \text{ kJ g}^{-1}$
	<i>trans</i> -2-Hydrindanone	<i>cis</i> -2-Hydrindanone
	37.8429	37.8256
	37.8394	37.8161
	37.8371	37.8259
	37.8254	37.8216
	37.8489	37.8262
	37.8351	
Mean	37.8381	37.8231
Standard deviation	0.0032	0.0019
		$-\Delta U_c^\circ/M = 37825.4 \text{ J g}^{-1}$

Table 3. Results and derived quantities at 25°C for *trans*-2-hydrindanone (I) and *cis*-2-hydrindanone (II).

	$\Delta U_c^\circ/\text{kJ mol}^{-1}$	$\Delta H_c^\circ/\text{kJ mol}^{-1}$	$\Delta H_f^\circ(\text{l})/\text{kJ mol}^{-1}$	$\Delta H_v/\text{kJ mol}^{-1}$	$\Delta H_f^\circ(\text{g})/\text{kJ mol}^{-1}$
I	-5229.64 ± 1.54	-5237.05 ± 1.54	-305.34 ± 1.62	56.1 ± 0.3	-249.2 ± 1.6
II	-5227.88 ± 1.20	-5235.29 ± 1.20	-307.10 ± 1.30	57.5 ± 0.3	-249.6 ± 1.3

more stable,^{2,13} but gave two different values for the isomerization enthalpy, about 8 and 18 kJ mol⁻¹. His result is based on combustion data for the liquid state from 1926.¹⁴ No details of the combustion measurements were available, so that no attempt has been made to recalculate the results in terms of modern energy units to enable comparison with the values reported in the present paper.

Thus, the 2-hydrindanones are intermediate between the hydrindanes,¹⁵ where the *trans*-isomer is the more stable, and the 8-methyl-2-hydrindanones,¹ where the more stable isomer is the *cis*. The difference between the hydrindanes

and the unsubstituted 2-hydrindanones is only just significant, however, if due regard is taken of the error limits associated with the enthalpy values.

Calculations on cyclic systems, using the Westheimer method,¹⁶ were referred to in the previous paper.¹ These calculations have now been improved, and although the results are preliminary, a clearer picture of the conformations and energies of the relevant molecules is becoming available.¹⁷ The results of these calculations apply strictly to the hydrocarbons, but there is some evidence that the substitution of an oxygen atom in or around a hydrindane ring system will have no large effect on the relative stabilities of *cis*- and *trans*-isomers.^{18,19} Introduction of a carbonyl group could, however, cause the small difference in relative stabilities between hydrindanes and 2-hydrindanones. The calculations indicate that in hydrindane systems with no bridge head substitution, the *trans*-isomer should be more stable by up to about 4 kJ mol⁻¹. There is an unfavourable axial substituent in the *cis*-form, and angle deformation in the *trans*-form, the balance being slightly in favour of the *trans*-isomer. Entropy is in favour of the *cis*-isomer,²⁰ and the equilibrium may lie in either direction, depending on the temperature. For the 8-methyl compounds, the calculations indicate that the *cis*-isomer should be the more stable by more than 4 kJ mol⁻¹ (experimental, 11.8 kJ mol⁻¹). In the *trans*-isomer, the 8-methyl group is pushed into the six-membered ring, increasing axial methyl-ring hydrogen interaction. In the *cis*-form, the methyl group is tipped away from the cyclohexane ring, leading to a small axial methyl interaction.

Thus, there is now fairly good agreement between energies and conformations for the hydrindane systems studied.

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