

Heats of Combustion of Propanal and 2-Methyl Propanal

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Heat of combustion values have been determined for propanal and 2-methyl-propanal and found to be, $\Delta H_c^\circ(\text{liq})$ at 25°C, -434.16 ± 0.18 kcal·mole⁻¹ and -589.67 ± 0.18 kcal·mole⁻¹, respectively. From these and previously published data, the C=O bond contribution in calculating heats of combustion by Klages' method has been found to be, on the average, 19.5 kcal.

Until recently accurate heats of combustion and formation data for alkanals have been lacking in the literature. Standard compilations have been using Berthelot's and Thomsen's values from the turn of the century^{1,2}. For formaldehyde³ and acrolein⁴ later values have been reported, although long before a modern reliable technique for the experimental determinations was established. In 1960 the present author reported the heats of combustion of two alkanals and two alkenals, and in the same year Nicholson published values for butanal and heptanal⁵. The work reported here gives data for two more alkanals, viz. propanal and 2-methyl-propanal.

The importance of approximate methods for the calculation of heats of combustion — and hence heats of formation — for aldehydes is still obvious, and the experimentally determined values have therefore been used to re-investigate the C=O bond contribution in the calculation of heats of combustion of aldehydes according to Klages' method⁶.

MATERIALS

Propanal. The commercial sample (Schuchardt) was distilled twice under nitrogen in a column of 35 theoretical plates (t.p.), the main fraction being the known azeotropic mixture of water and propanal⁷. The purification was followed by use of gas-liquid chromatography (GLC) (column 25 % tricresylphosphate on C22, $t = 50^\circ$, ionization detector) and already the azeotrope was found to be free from organic impurities. The product was dried three times with anhydrous calcium sulphate and then distilled under nitrogen in a column of 10 t.p. Four middle fractions, which all showed the same boiling point

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Table 1. Propanal

Water content of compound = 0.03 %.

 $m(\text{Pt}) = 23.781 \text{ g}$, $m^i(\text{cont}) = 36.23 \text{ g}$, $\epsilon^i(\text{cont}) = 3.85 \text{ cal}\cdot\text{deg}^{-1}$, $\Delta E_{\Sigma} = 1.70 \text{ cal}$.

m' g	m'' g	m''' g	Δt deg	$\Delta E(\text{HNO}_3)$ cal	$-\Delta E'_c/M$ cal·g ⁻¹
0.373625	0.226378	0.004465	0.89818	3.65	7460.66
0.361782	0.229433	0.004865	0.88906	3.69	7458.91
0.369292	0.227385	0.004290	0.89452	3.55	7461.90
0.374259	0.227169	0.003979	0.89991	3.21	7458.39
0.370056	0.223179	0.004910	0.88822	3.64	7464.06
0.373431	0.220557	0.004816	0.88758	3.56	7464.89
			Mean		7461.47
			Stand. dev. of mean		1.09

$$\Delta E'_c/M = -7461.5 \text{ cal}\cdot\text{g}^{-1}$$

$$\Delta E_c/M = -7463.7 \text{ cal}\cdot\text{g}^{-1}$$

Table 2. 2-Methyl-propanal

 $m(\text{Pt}) = 23.841 \text{ g}$, $\epsilon^i(\text{cont}) = 3.85 \text{ cal}\cdot\text{deg}^{-1}$, $\Delta E_{\Sigma} = 2.10$ except in the last combustion where $\Delta E_{\Sigma} = 1.71 \text{ cal}$.

m' g	m'' g	m''' g	$m^i(\text{cont})$ g	Δt deg	$\Delta E(\text{HNO}_3)$ cal	$-\Delta E'_c/M$ cal·g ⁻¹
0.466268	0.121188	0.004951	36.29	0.87549	3.67	8164.70
0.480440	0.115596	0.004666	36.29	0.88442	3.20	8164.68
0.447774	0.149216	0.005008	36.30	0.90200	3.03	8164.30
0.465133	0.128884	0.004874	36.30	0.88812	3.12	8164.80
0.379532	0.188615	0.004934	36.27	0.88096	2.68	8167.59
				Mean		8165.21
				Stand. dev. of mean		0.60

$$\Delta E'_c/M = -8165.2 \text{ cal}\cdot\text{g}^{-1}$$

Table 3. Thermochemical data at 25°C, in kcal·mole⁻¹.

Compound	$-\Delta H_c^{\circ}(l)$	$-\Delta H_f^{\circ}(l)$	ΔH_v^*	$-\Delta H_c^{\circ}(g)$	$-\Delta H_f^{\circ}(g)$
Propanal	434.16 ± 0.18	52.95 ± 0.18	7.1	441.3	45.9
Butanal	592.42 ± 0.34	57.06 ± 0.34	8.1	600.5	49.0
2-Methyl-propanal	589.67 ± 0.18	59.81 ± 0.18	7.7	597.4	52.1
2-Ethyl-hexanal	1215.63 ± 0.36	83.32 ± 0.36	11.3	1226.9	72.0
2-Butenal	546.71 ± 0.18	34.45 ± 0.18	9.2	555.9	25.3
2-Ethyl-2-hexenal	1168.17 ± 0.34	62.46 ± 0.34	11.7	1179.9	50.8

The given uncertainties are twice the final overall standard deviations¹³.* Estimated by Klages' formula: $\Delta H_v(25^{\circ}\text{C}) = (5.4 + 0.036t_{\text{B}}) \text{ kcal}\cdot\text{mole}^{-1}$.

Table 4. The C=O bond contribution in heats of combustion of alkanals.

Alkane	Alkanal	$-\Delta H_c^\circ(\text{alkane})$ kcal.mole ⁻¹	$-\Delta H_c^\circ(\text{alkanal})$ kcal.mole ⁻¹	$\lambda(\text{C=O})$ kcal.
Propane	Propanal	530.60	441.3	18.7
Butane	Butanal	687.64	600.5	20.9
2-Methyl-propane	2-Methyl-propanal	685.64	597.4	19.8
3-Methyl-heptane	2-Ethyl-hexanal	1316.44	1226.9	18.5
			Mean	19.5

and density, were combined and used in the combustion experiments. B.p. = 47.85°C/760 mm, $d_4^{25} = 0.7919$. From a melting curve (m.p. = -103.0°C) the residual amount of water was estimated to be 0.03 ± 0.02 %.

2-Methyl-propanal. By distilling twice a commercial sample (Light) in the column with 35 t.p. a pure product was obtained. The first fractions from the first distillation contained much water and the last ones fairly large amounts of high boiling substances. A very small fraction, 1/8 of the charge, ($d_4^{25} = 0.7821$) was used in the second distillation, from which half the amount was collected in fractions showing constant density and b.p. Nevertheless, only a small middle fraction was used for the combustion, b.p. = 64.34°C/760 mm, $d_4^{25} = 0.7823$. No impurities could be detected by GLC (column 20 % LAC 3R-728 on C22, $t = 50^\circ$, ionization detector), and the melting curve (m.p. = -72.15°C) indicated that the total amount of water was less than 0.01 %.

COMBUSTION CALORIMETRY

All calorimetric results are expressed in terms of the defined calorie, which is equal to 4.1840 abs. joules. All weighings have been reduced to mass, and the molecular weights are based upon the 1957 International Atomic Weights. In this work the symbols and calculating procedure introduced by Hubbard, Scott and Waddington⁸ have been used.

Apparatus and method. A static, platinum lined bomb⁹ was used in the calorimeter described by Bjellerup¹⁰. The calibration experiments have been published elsewhere¹¹.

The aldehydes were burnt in soft glass ampoules with paraffin oil as combustion aid. The volatility and explosiveness of propanal made it necessary to use small ampoules, and therefore only 50 % of the total amount of heat evolved originated from the propanal. For 2-methylpropanal the corresponding figure was ca. 75 %. The amount of nitric acid formed in each combustion was determined by titration with sodium hydroxide.

The results of the combustion experiments are reported in Tables 1 and 2. Common to the two tables are the following values:

$$\begin{aligned} \varepsilon^\circ(\text{calor}) &= 5\,930.59 \pm 0.27 \text{ cal.deg}^{-1}, t_h = 25.0^\circ\text{C}, t_i = 24.1^\circ\text{C}, \\ P^i(\text{Gas}) &= 30.0 \text{ atm}, V(\text{Bomb}) = 0.2751 \text{ l}, V^i(\text{Water}) = 0.820 \text{ ml}, \\ \Delta E_c^\circ/M(\text{Oil}) &= -10\,986.6 \pm 0.6 \text{ cal.g}^{-1} \text{ and } \Delta E_c^\circ/M(\text{Fuse}) = -3\,971 \pm 4 \\ &\text{cal.g}^{-1}. \end{aligned}$$

Correction for the water content of propanal has been made.

Results. From the found $\Delta E_c^\circ/M$ values, ΔH_c° and ΔH_f° values were calculated. Final overall standard deviations were computed as given elsewhere⁹. Using Klages' formula¹², heats of vaporization data were estimated, and heats of formation and combustion data for the compounds in the gaseous state were derived. Table 3 gives these values for all the aldehydes studied.

DISCUSSION

Although not so many aldehydes have been studied, the data obtained are sufficient to calculate an average value for the C=O bond contribution to estimated heat of combustion data for aldehydes using Klages' method⁶.

In order to eliminate possible structural effects, the following method has been used in the calculations. From the heat of combustion of an appropriate alkane two C—H bond contributions, $\lambda(\text{C—H})$, are subtracted, and one C=O bond contribution, $\lambda(\text{C=O})$, is added, whereby the heat of combustion of the corresponding aldehyde is obtained.

$$-\Delta H_c^\circ(\text{alkane, g}) - 2\lambda(\text{C—H}) + \lambda(\text{C=O}) = -\Delta H_c^\circ(\text{alkanal, g})$$

The heat of combustion values for the alkanes have been taken from Rossini¹⁴, and Klages' value for $\lambda(\text{C—H}) = 54.0$ kcal has been used. Table 4 gives the results for the four alkanals studied.

Thus, a strict method of comparison has been used, but nevertheless, the values obtained vary surprisingly. The reason for this is obscure, and it might be argued that the high value for butanal could be due to a systematic error in its heat of combustion value. However, this datum was recently reported by Nicholson⁵, who found $\Delta H_c^\circ(\text{butanal, l}) = -592.05 \pm 0.34$ kcal.mole⁻¹ in close agreement with the value used here (*cf.* Table 3).

From the values in Table 3, the heats of hydrogenation of the olefinic bonds in 2-butenal and 2-ethyl-2-hexenal were calculated to be -23.7 ± 0.5 and -21.2 ± 0.5 kcal.mole⁻¹, respectively. Rossini and Rockenfeller¹⁵ have given average values for the heats of hydrogenation of olefinic bonds in different intramolecular environments, and for a *trans* 1,2-dialkylethene their value is -27.0 and for a 1,1,2-trialkylethene -26.4 kcal.mole⁻¹, respectively. The difference between the two sets of values is 3.3 and 5.2 or, on the average, 4.2 kcal.mole⁻¹, which then represents the conjugation stabilization energy in the unsaturated aldehydes. Kistiakowsky and coworkers reported in 1938 the heat of hydrogenation of 2-butenal at 82°C, without giving details of the purity of the compound¹⁶. Recalculated to 25°C their value becomes 24.8 kcal.mole⁻¹, which is in reasonable agreement with the present result.

In conclusion it might be said that structural effects seem to be more pronounced in alkanals and alkenals than in alkanes or monofunctionally substituted alkanes. Only further work can reveal to what extent this statement is justified.

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