

HEATS OF COMBUSTION OF BUTANAL AND SOME RELATED COMPOUNDS*

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Precision data on heats of combustion of aliphatic aldehydes are lacking in the literature and since the appearance of Kharasch's compilation¹ no further determinations have been published. Therefore it was judged of interest to study a number of aliphatic aldehydes. The choice of compounds was mainly governed by an interest in the aldol condensation reaction and associated processes for butanal.

SAMPLE PURITY

It is a well-known fact that simple aliphatic aldehydes are difficult to obtain in a very pure state and this work has given no evidence for expressing an opposite opinion. Before describing the special problems met with in handling the aldehydes, the general procedure for preparing the samples for combustion will be given.

Procedure

All six substances used in this investigation were prepared and carefully purified by the Research Laboratory, Mo and Domsjö Aktiebolag, Örnsköldsvik, Sweden. After the final distillation in a Podbielniak column with 50-70 theoretical plates, samples of the main fraction were enclosed in sealed Pyrex-glass ampoules in an atmosphere of nitrogen or helium. On the contents of one of these ampoules the purity was established using gas-liquid chromatography, and a number of ampoules were sent without delay to our laboratory. Immediately upon arrival (2-3 days later) a distillation was performed at room temperature under reduced pressure. All samples were handled in a nitrogen atmosphere and utmost care was taken to exclude air. The middle fraction from this distillation (about one-third of the total sample) was collected in a receiver where some ten combustion ampoules (made from soft glass) had been placed in advance, and these were immediately sealed². At the same time ampoules were filled with samples for gas-liquid chromatographic analysis and for density determination. The combustions were made as soon as possible, and in no case more than six days elapsed between ampoule filling and the last combustion. In the case of butanal all experiments were carried out within two days. Analysis (by Mo and Domsjö) and density determination were performed so as to coincide in time with the middle experiment in the combustion series.

The gas-liquid chromatographic analysis was done in order to determine the amount of impurities, especially water. For all substances except butanal the area under the water peak on the chromatogram was pro-

*Published in *Acta Chem. Scand.*, **14**, 180 (1960)

portional to the water content of the sample, which was found from calibration experiments with known amounts of water added to the sample. The linearity implies that no reaction leading to the formation of water occurred on the column. In the case of butanal, however, a reaction took place on the column with formation of water.

The water content of the butanal sample was evaluated using the observation that the density of a sample of this compound varied linearly with the water content, at least over a small range. A sample of butanal was prepared exactly as the material for combustion. This sample was divided into three parts and water was added to two of them, increasing the amount of water by 0.275 and 0.551 per cent, respectively. The densities of the three parts were determined (*Table 1*).

Table 1. Density and water content of butanal

Water (%)	d_4^{25} (g/ml)
x	$0.7966_0 \pm 0.0000_2$
$x + 0.275$	$0.7976_1 \pm 0.0000_3$
$x + 0.551$	$0.7988_2 \pm 0.0000_3$

The slope of the line, density *versus* per cent water, was calculated, and a line was drawn using the value of Smith and Bonner³: $d_4^{25} = 0.7964$ at 0.03 per cent of water. The density 0.7966 then corresponds to a water content of 0.08 ± 0.02 per cent.

Special problems

The unsaturated aldehydes studied were found to be stable during storage in Pyrex ampoules for two weeks. However, distillation at temperatures higher than *ca.* 50°C caused rapid decomposition. The sensitivity towards oxidation was found to be very pronounced, and it was therefore necessary to exclude even traces of air in handling these compounds. Butanal was found to be unstable even when every precaution was taken in storing the samples. The decomposition was followed by measuring the density, and an increase in d_4^{25} of 0.00003 per day was observed. Distillation of butanal above room temperature caused an increase in water content and in amounts of other impurities. When distillation was performed at room temperature with the receiver kept at -40° to -80°C, the distillate showed a marked tendency to polymerize to solid products. A few successful distillations were performed with the receiver kept at -20°C and the distilling flask at 35°C (pressure 40–50 mm Hg).

In a number of cases condensation of butanal took place within the combustion ampoule, which then invariably burst. This was shown by the following series of experiments. Twelve ampoules (of the combustion type) were filled with butanal and left to stand for some days. During this time several ampoules burst. Now and then one of the intact ampoules was opened, and in both cases the refractive index of the content was immediately determined. The refractive index of the content was unchanged for all intact ampoules, but had altered for every broken ampoule, usually by about 0.002 units.

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2-Ethylhexanal offered the same kind of handling difficulties as did butanal but to a much smaller extent. Distillation could be performed at 85°C and 35 mm Hg, and gas-liquid chromatograms were successfully run at 150°C. With the alcohols of this investigation no special problems were met, and the analyses showed that perfect purity was obtained in both cases.

Results of purity determinations

In *Table 2* values of densities and amounts of impurities have been summarized. For comparison, density values found in the literature have also been given.

Table 2. Sample purity

<i>Substance</i>	d_4^{20} (g/ml)	d_4^{25} (g/ml)	H ₂ O (%)	Org. (%)	<i>Literature</i>
2-Butenal	0.8526	0.8475	0.02	0.05	$d_4^{17.3} = 0.8557^{(4)}$
Butanal	—	0.7966	0.08	—	$d_4^{23} = 0.7964$ (0.03% H ₂ O ⁽³⁾)
1-Butanol	0.8099	0.8059	0	0	$d_4^{25} = 0.8057^{(6)}$
2-Ethylhex-2-enal	0.8522	0.8461	0.014	0.4	$d_4^{20} = 0.8528^{(6)}$
2-Ethylhexanal	0.8201	0.8156	0.03	0.7	$d_4^{18} = 0.8231^{(7)}$
2-Ethylhexan-1-ol	0.8332	0.8291	0	0	$d_4^{20} = 0.8328^{(8)}$

COMBUSTION CALORIMETRY

The calorimeter described by Bjellerup⁹ was used without rotation of the bomb. Washburn corrections have been applied as described by Hubbard, Scott and Waddington¹⁰; the latter's procedure and the nomenclature given by them have been followed. Corrections for the water content of the samples have been applied.

Table 3. Thermochemical data, referring to the liquid standard state at 25°C*

<i>Substance</i>	$-\Delta E_c^\circ$ (kcal/mole)	$-\Delta H_c^\circ$ (kcal/mole)	$-\Delta H_f^\circ$ (kcal/mole)
2-Butenal	546.12 ± 0.09	546.71 ± 0.09	34.45 ± 0.09
Butanal	591.53 ± 0.17	592.42 ± 0.17	57.06 ± 0.17
1-Butanol	637.07 ± 0.10	638.25 ± 0.10	79.55 ± 0.10
2-Ethylhex-2-enal	1166.39 ± 0.17	1168.17 ± 0.17	62.46 ± 0.17
2-Ethylhexanal	1213.56 ± 0.18	1215.63 ± 0.18	83.32 ± 0.18
2-Ethylhexan-1-ol	1261.44 ± 0.19	1263.81 ± 0.19	103.46 ± 0.19

* The uncertainties given are the final overall standard deviations.

The final overall standard deviations include the errors of (1) the heat of combustion value for benzoic acid, (2) the calibration experiments, (3) the paraffin oil combustions, (4) the determination of weight including water analysis and finally (5) the standard deviation of the actual combustion series.

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