

HEATS OF COMBUSTION AND ENTHALPIES OF FORMATION OF D-RIBOSE, D-ARABINOSE, AND L-ASCORBIC ACID

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ABSTRACT

The standard enthalpies of formation at 25°C derived from observed heats of combustion are L-ascorbic acid, $\Delta H_f^0(c) = -278.34 \pm 0.24 \text{ kcal} \cdot \text{mole}^{-1}$; D-ribose, $\Delta H_f^0(c) = -251.16 \pm 0.17 \text{ kcal} \cdot \text{mole}^{-1}$; and D-arabinose, $\Delta H_f^0(c) = -252.84 \pm 0.39 \text{ kcal} \cdot \text{mole}^{-1}$.

INTRODUCTION

The quantitative study of the energetics of biochemical reactions requires an accurate knowledge of the thermochemical properties of the reacting compounds. The extent of such data is still quite limited. Values of the heats of combustion, using modern equipment and techniques, are reported for three important carbohydrates. From these results, the enthalpies of formation of the three pure crystalline compounds in the standard state at 25°C have been derived.

EXPERIMENTAL

High purity grades of commercial samples were used in the combustion studies. The sources were: D-ribose (California Corporation for Biochemical Research, Grade A), D-arabinose (Eastman Organic Chemical, White Label), and L-ascorbic acid (Fischer Reagent Grade). Except for drying, the samples were burned as received. Thermogravimetric studies showed no evidence of decomposition of arabinose or ascorbic acid below 150°C, or of ribose below 100°C. This was confirmed by the DTA curves of Perkins and Mitchell¹ for ribose and arabinose. Studies of Comer and Howell² show that the rate of decomposition of ascorbic acid is negligible for the conditions used for drying. After compressing each sample into a pellet, it was dried to constant weight by exposure to silica gel at pressures of less than one millimeter of mercury. Arabinose and ascorbic acid were kept at 55°C during this time, and ribose was kept at 25°C. 80–90 h of such treatment were required.

The compounds were burned in a Parr Instrument Company 1106 bomb which was initially filled with oxygen at $30.00 \pm 0.01 \text{ atm}$. Combustible impurities were removed from the oxygen by passing it through a furnace packed with copper

oxide at 500°C. 1 g of water was placed in the bottom of the bomb to give a water-saturated gas phase. The pellets were weighted to an accuracy of 0.05 mg and corrections for air buoyancy were applied. The loaded bomb was placed in a Precision Scientific Company 3028 calorimeter, and the initial temperature of the water in the bucket was adjusted to within 0.002 of 25°C. The water in the jacket was adjusted to within 0.02 of 27.34°C and then held constant to within 0.002° during any one experiment. Ignition was accomplished by an iron wire fuse which produced 8.2 cal, as determined by blank runs.

The temperature of the water in the calorimeter bucket was measured with a Leeds and Northrup knife-type platinum resistance thermometer. The resistance was measured with a Leeds and Northrup G2 Mueller Bridge and Keithly 147 electronic null detector. The thermometer had a resistance of 28.0545 Ω at 25°C and a coefficient of 9.921 °C per Ω . In order to follow the temperature of the calorimeter, the times were recorded when the indicator of the null detector passed through zero following equal increments in the bridge setting. This procedure established the final temperature relative to the initial temperature reproducibly to within at least 5×10^{-5} degrees.

Attempts to burn pellets of the three compounds alone in the bomb were not successful. Some soot was always left. However, when placed in contact with a pellet of benzoic acid weighing in the range of 0.2–0.9 g, the samples usually burned completely to carbon dioxide and water. Results of experiments in which this was not achieved were discarded. In addition to carbon dioxide and water, a small quantity of nitric acid, derived from the nitrogen present as an impurity in the oxygen, was formed. The resulting solution was titrated with standard sodium hydroxide to determine the quantity of nitric acid produced and an appropriate correction was applied. The combustions produced temperature increases in the range of 1.9–2.4 degrees. The effective thermal conductivity between jacket and calorimeter was always in the range of $(1.59 \pm 0.02) \times 10^{-3} \cdot \text{min}^{-1}$.

The effective energy equivalent of the empty calorimeter was determined by burning benzoic acid sample 39i obtained from the National Bureau of Standards. The heat of combustion was certified as 26,434 abs. J·g⁻¹ when burned under certificate conditions. The average of ten calibration runs was 46601.2 cal· Ω^{-1} , with 6.0 cal· Ω^{-1} for twice the standard deviation of the mean. Benzoic acid sample 39i was also used as an auxiliary material to aid in the combustion of the carbohydrate samples. Heats of combustion and formation based on weights of samples are reported in units of the defined calorie (4.184 J exactly). The molecular weights shown in Table II are based on the 1961 atomic weights. The 1963 fundamental constants were used throughout.

All calculations, including conversion of temperature and time measurements to initial and final temperatures, corrections for stirring energy and heat exchange between calorimeter and jacket, and reductions to the standard state, were carried out on a digital computer programmed to follow the procedure of Hubbard, Scott, and Waddington³. Auxiliary data used in these calculations are: density, 1.585 g·cm⁻³ for arabinose and ribose and 1.650 g·cm⁻³ for ascorbic acid; specific heat,

0.291 cal·degree⁻¹·g⁻¹; and an energy coefficient, -5×10^{-3} cal·atm⁻¹·g⁻¹, for all three compounds. Table I lists pertinent experimental and intermediate quantities for a typical run for each of the three compounds.

TABLE I
OBSERVED DATA FOR SAMPLE COMBUSTION EXPERIMENTS

Characteristics	D-Arabinose	D-Ribose	L-Ascorbic acid
Mass of sample, m_1 (g)	1.83135	1.68187	2.08119
Mass of benzoic acid, m_2 (g)	0.31231	0.57467	0.35892
Initial temperature of calorimeter, t_1 (Ω)	28.054356	28.054362	28.054405
Heat exchange correction, t_{corr} (Ω)	0.001386	0.000702	0.001342
Corrected final temperature, $t_f - t_{\text{corr}}$ (Ω)	28.243178	28.267147	28.245203
Moles of nitric acid formed, $n^f(\text{HNO}_3)$	1.80×10^{-4}	1.80×10^{-4}	1.61×10^{-4}
Correction for nitric acid, $\Delta E_{\text{decomp}}^f(\text{HNO}_3)$ (cal)	2.53	2.53	2.26
Isothermal bomb energy, ΔE_B (cal)	-8800.74	-9918.78	-8892.67
Combustion of benzoic acid, ΔE_c (cal)	-1971.61	-3727.89	-2265.86
Correction to standard state, ΔE_x (cal)	7.81	8.86	10.29
Energy of combustion at 25°C, $\Delta E_c^0/M$ (cal·g ⁻¹)	-3723.37	-3733.64	-3178.11

RESULTS

Table II summarizes the results of a series of successful combustions. The average heat of combustion, $\Delta E_c^0(c)/M$, and the value of 2σ (σ = standard deviation of the mean) are shown. The standard state enthalpy of combustion to liquid water

TABLE II
FINAL VALUES OF ENTHALPIES OF COMBUSTION AND FORMATION

Characteristics	L-Ascorbic acid (C ₆ H ₈ O ₆)	D-Ribose (C ₅ H ₁₀ O ₅)	D-Arabinose (C ₅ H ₁₀ O ₅)
Molecular weight	176.13	150.13	150.13
Number of determinations	5	5	6
$\Delta E_c^0/M$ (cal·g ⁻¹)	-3178.50	-3734.51	-3723.33
2σ (cal·g ⁻¹)	1.08	0.33	2.38
$\Delta H_c^0(c)$ (kcal·mole ⁻¹)	-559.23 ± 0.23	-560.67 ± 0.15	-558.99 ± 0.38
$\Delta H_f^0(c)$ (kcal·mole ⁻¹)	-278.34 ± 0.24	-251.16 ± 0.17	-252.84 ± 0.39

and gaseous carbon dioxide, $\Delta H_c^0(c)$, was calculated from $\Delta E_c^0(c)/M$. The uncertainties listed include the effect of uncertainty in the heat of combustion of the benzoic acid used as an auxiliary material and the uncertainty in the energy equivalent of the calorimeter, in addition to the effect of 2σ for the series of combustions. They do not include the possible effects of water or other impurities in the samples. Enthalpies of formation were calculated based on the standard values of $\Delta H_f^0(\text{H}_2\text{O}, \text{l}) =$

$-68.315 \text{ kcal}\cdot\text{mole}^{-1}$ and $\Delta H_f^0(\text{CO}_2, \text{g}) = -94.051 \text{ kcal}\cdot\text{mole}^{-1}$ derived from the measurements of Rossini⁴, and Prosen and Rossini⁵. The corresponding uncertainty includes the effect of uncertainties in these quantities.

A series of preliminary combustions of ascorbic acid by one of the authors (R. C. W.) with another calorimeter gave an average $\Delta E_c^0/M$ of $-3161.9 \text{ kcal}\cdot\text{g}^{-1}$. Since these samples were not dried as thoroughly as the ones reported in Table II, the low value very probably was caused by the presence of water in the samples. Two earlier measurements of the heat of combustion of D-arabinose differing by more than $1.5 \text{ kcal}\cdot\text{mole}^{-1}$ have been reported in the literature. When converted to modern units, Stohman and Langbein⁶ obtained $\Delta H_c^0(c) = -558.2 \text{ kcal}\cdot\text{mole}^{-1}$ and Karrer and Fioroni⁷ obtained $\Delta H_c^0(c) = -559.8 \text{ kcal}\cdot\text{mole}^{-1}$. More recently Stroh and Fincke⁸ reported $\Delta H_c^0(c) = -557.89 \pm 1.09 \text{ kcal}\cdot\text{mole}^{-1}$ for D-ribose which is appreciably lower than the result listed in Table II. Since they gave very few experimental details, it is difficult to assign a reason for their lower value. In view of the difficulty of drying these compounds, their lower result may be due to the presence of water in the combustion samples.

Furberg and Hordvik⁹ have determined the crystal structure of β -D-arabinose by X-ray diffraction. They found that the pyranose ring is present in a staggered chair form. Ribose probably has a very similar structure except that the hydroxyl group attached to carbon atom number 1 is in the axial rather than the equatorial position. This places the oxygen atoms of the $-\text{OH}$ groups on carbon atoms 2 and 3 much closer to the oxygen atom in the ring in ribose than in arabinose. In the gas phase this would cause the heat of formation of ribose to be more positive than that of arabinose. Although this prediction is less certain for the crystalline states, it was found nevertheless that $\Delta H_f^0(c)$ is $1.68 \text{ kcal}\cdot\text{mole}^{-1}$ more positive for D-ribose than for D-arabinose.

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