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Enthalpies of Combustion of Organic Compounds. II. L- and D-Glutamic Acid

Minoru SAKIYAMA and Syûzô SEKI

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

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Synopsis. Enthalpies of combustion of L- and D-glutamic acid in the crystalline state have been measured by oxygen bomb calorimetry. Standard enthalpies of formation at 298.15 K have been determined.

Among optically active aliphatic amino acids, the enthalpy of combustion has been determined for both isomers in few compounds. The only exception is leucine in the crystalline state and the values obtained by Huffman *et al.*[1] of both isomers coincide with each other. In this paper the enthalpies of combustion of L- and D-glutamic acid in the crystalline state are reported. The idealized combustion reaction to which the energies and enthalpies of combustion refer is the following one at 25 °C:

$$C_5H_9O_4N(c) + 5.25O_2(g) = 5CO_2(g) + 4.5H_2O(l) + 0.5N_2(g).$$

Materials. L-Glutamic acid (Takara Kōsan Co. Ltd.) and D-glutamic acid (Ajinomoto Co. Ltd.) were purified by recrystallization from aqueous solution. Crystals were dried, pelletted and stored on silica gel for at least 72 h before combustion. X-Ray diffraction using Cu-Kα radiation shows that the crystals belong to the β-phase[2] (the most stable modification).

Apparatus, Procedures and Calculations. An isoperibol, rotating, precision bomb-calorimeter[3] was used without rotation. In order to facilitate complete combustion of the samples, *ca.* 0.2 g of liquid paraffin (Wakō Pure Chemical Co. Ltd.) was used as an auxiliary oil. No weight loss was observed when the liquid paraffin was placed in an open dish in air for several hours. The standard energy of combustion of the oil was determined by six combustion experiments. The results of the individual combustion experiments in term of $\Delta E_c^\circ/M$ at 298.15 K are −45909.9, −45924.5, −45905.4, −45913.0, and −45909.4 J g^{-1}. Mean and standard deviations of the mean are −45909.3±4.1 J g^{-1}. Calorimetric procedures and methods of calculation are similar to those described previously.[3] The energy equivalent of the standard calorimetric system[3] was found from six calibration experiments by using benzoic acid (Standard Reference Material 39i, National Bureau of Standards, U.S.A) to be 15164.4±0.8 J K^{-1}, where the uncertainty is the standard deviation of the mean.

Auxiliary Quantities. The molecular weights were computed on the basis of the 1961 table of atomic masses. The composition formula and the values (for 25 °C) of density, ρ, specific heat capacity, c_p, and $(\partial E/\partial p)_T$ for the combustible substances are given in Table 1. Two crucibles were used. One (#1, wt. 11.141 g) is made of Pt-10% Rh alloy with density and specific heat capacity of 20.50 g cm^{-3} and 0.1464 J K^{-1} g^{-1}, respectively, at 25 °C. The other (#2, wt. 11.137 g) is made of platinum with density and specific heat capacity of 21.40 g cm^{-3} and 0.1362 J K^{-1} g^{-1}, respectively, at 25 °C.

Table 1. Auxiliary quantities used in the calculation of standard energy of combustion

	ρ / g cm^{-3}	c_p / J K^{-1} g^{-1}	$(\partial E/\partial p)_T$ / J kPa^{-1}g^{-1}
L- and D-Glutamic acid $C_5H_9O_4N$	1.538	1.19	(−0.60)[a]
Auxiliary oil $CH_{1.855}$	0.882	2.22	−2.60
Fuse $CH_{1.860}O_{0.930}$	1.5	1.70	−2.94

a) Estimated value.

Results

Six combustion experiments were carried out with L- and D-glutamic acid. Data from combustions selected as typical are given in Table 2. Notations follow those given by Hubbard *et al.*[5] except for the following: Δm (H_2O cal.), excess water in the calorimeter can; ΔE (std. state), sum of items 81—85, 87—89, 93, and 94 in ref. 5. Results of the individual combustion experiment in terms of $\Delta E_c^\circ/M$ at 298.15 K are summarized as follows: −15298.6, −15293.1, −15293.8, −15307.3, −15299.3, −15307.1, mean and standard deviation of the mean −15300.3±2.5 J g^{-1} for L-glutamic acid and −15304.3, −15304.0, −15309.2, −15301.5, −15309.7,

Table 2. Typical combustion experiments

	L-Glutamic acid	D-Glutamic acid
m^i(compd.)/g	1.16927	1.17672
m^i(auxil. oil)/g	0.20518	0.19690
m^i(fuse)/g	0.00265	0.00234
m^i(H_2O tot.)/g	1.081	1.090
m^i(Pt)/g	11.141	11.157
Δm^i(H_2O cal.)/g	−0.074	0.104
P^i(gas)/MPa	3.040	3.040
T_i/°C	23.15799	23.17928
T_f/°C	24.98876	24.99227
ΔT_{corr}/°C	0.02458	0.02448
$n^f(HNO_3)$/mol	0.000793	0.000815
ΔE_{ign}/J	5.60	5.78
$\Delta E_{dilu}(HNO_3)$/J	−0.11	−0.12
$\Delta E_{decomp}(HNO_3)$/J	46.69	48.00
ΔE(std. state)/J	17.71	17.70
ε^i(cont.)/J K^{-1}	18.17	18.08
ε^f(cont.)/J K^{-1}	20.39	20.28
ΔE_c°/J g^{-1}	−15299.3	−15301.5

Table 3. Thermodynamic quantities of L- and D- glutamic acid

	ΔE_c° / kJ mol^{-1}	ΔH_c° / kJ mol^{-1}	ΔH_f° / kJ mol^{-1}
L-Glutamic acid	-2251.09 ± 0.93	-2250.47 ± 0.93	-1003.32 ± 1.16
D-Glutamic acid	-2251.94 ± 0.68	-2251.32 ± 0.68	-1002.47 ± 0.97

-15305.1, mean and standard deviation of the mean -15305.6 ± 1.3 J g^{-1} for D-glutamic acid. Thermochemical quantities have been calculated from these results and are given in Table 3. In the calculation of the standard enthalpies of formation, CODATA key values[6] were employed for the standard enthalpy of formation of $H_2O(l)$ and $CO_2(g)$. Uncertainties in Table 3 are uncertainty interval recommended by Rossini,[7] *i. e.*, twice the final overall standard deviation of the mean.

Discussion

The difference in the standard enthalpies of combustion of L- and D-glutamic acids as observed in the present work is 0.85 kJ mol^{-1}, which is 0.038% of the ΔH_c° values and well within the sum of each uncertainty interval. It may be stated that no difference is found between the enthalpy of combustion values of L- and D-glutamic acid within the limit of precision of the present work.

The enthalpy of combustion of L-glutamic acid has been reported by Fischer and Wrede,[8] Emery and Benedict,[9] Huffman *et al.*,[10] Oka,[11] and Tsuzuki and Hunt.[12] In compilations published recently,[13,14] Tsuzuki's value[12] ($\Delta H_c^\circ=-2244.09\pm0.75$ kJ mol^{-1}, where uncertainty is the uncertainty interval) is adopted as a selected value. The present result on L-glutamic acid is in agreement with that of Huffman *et al.*[10] ($\Delta H_c^\circ=-2248.52\pm1.17$ kJ mol^{-1}, where uncertainty is the uncertainty interval) within the assigned uncertainty intervals, while the present result is 6.3 kJ mol^{-1} more negative than the selected value mentioned above. Nothing has ever been reported on the enthalpy of combustion of D-glutamic acid.

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